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A STUDY OF THE POLARIZATION UPON A THIN METAL PARTITION IN A VOLTAMETER. I.

By John Daniel.

Introduction.

THE curious polarization phenomena of very small electrodes in a sulphuric acid voltameter bearing a strong current, accounts of which appeared in the *Annalen* during the winter of 1892, suggested to Dr. L. Arons, of the University of Berlin, to try a very thin metal partition in a voltameter — expecting, as he said, that there would be a development of heat at this partition, resulting in the destruction of the partition. Dr. Arons used gold-leaf as a partition. The gold-leaf was pasted with Canada balsam over a hole about 15 mm. in diameter bored in a glass plate, which was slipped into the groove of a wooden or vulcanite frame in the middle of the voltameter. This did not give a tight partition, but sufficed for the observation that there was not even visible development of gas on the gold-leaf; whereas platinum 0.02 mm. thick substituted for the gold-leaf showed profuse development of gas with the current strength used, even when punctured with a hole 2 mm. square. I think Dr. Arons also tried the gold-leaf partition in a solution of a salt of copper or of silver, and observed that the metal was deposited on the partition.

At the suggestion and under the kind direction of Professor A. Kundt and Dr. L. Arons, I undertook a more thorough investigation of the subject.

Several problems presented themselves: —

(1) By quantitative measurement to determine whether there be a critical thickness below which there will be no polarization at the partition, and if so, to determine this thickness.

(2) To determine the other critical thickness for which the polarization is as great as for very thick plates.

(3) The quantitative measurement of this polarization with the same current strength for plates of various thicknesses between these limits.

(4) By varying the current strength in these different cases, to determine what function the polarization is of the current strength.

(5) To learn how the polarization in these cases varies with the time during which a given current strength flows, readings being made periodically until the polarization becomes constant, or nearly so.

These are the principal direct problems that have been attacked. Numerous minor observations have been made and will be discussed in their place. The experiments have been made in a room of fairly constant temperature, and no attempt has been made to account for slight variations of temperature as affecting resistance, etc., as the quantities to be measured are interesting mainly as regards their relative values; but especially because so slight a correction would be cloaked by such unavoidable variations as irregular escape of gas from the electrodes or partition, in case of its development there.

Apparatus.

The instruments employed, as well as the plan of the experiments, are very simple. As a galvanoscope, as well as current measurer, a well-damped ring galvanometer was used. The galvanometer has four coils of about 22 ohms each, which may be connected as desired. Deflections were read with a telescope from a scale divided into millimeters, fixed at a distance of 1.5 m. The

instruments are supported by an independent stone pier. As nearly as possible the same deflection of the galvanometer was always used, the resistance being so adjusted as to effect this, and the "figure of merit" of the galvanometer for this position was determined by connecting a Daniel cell with the galvanometer in series with a known resistance of such value as to give the deflection to be used, and found to be, by Ohm's law,

$$\gamma = 0.000000265 \text{ ampere per scale division.}$$

For another position used later, $\gamma = 0.000000224$.

The connections for the galvanometer circuit are shown in Fig. 1, in which B is a battery of storage cells, V the voltameter (with partition a), C a commutator, G the galvanometer (with key k). R is an auxiliary resistance in the main circuit, r_1 a resistance with which the galvanometer is in shunt, ρ an auxiliary resistance of 1010 ohms. The total resistance in the galvanometer circuit is 1100 ohms. I is the main current in amperes; i_1 and i_2 are the currents in the branch circuits.

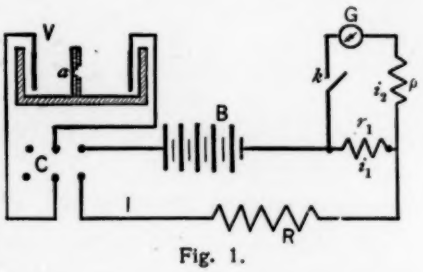

Fig. 1.

To measure the strength of current flowing through the voltameter at any time, we observe the scale deflection, and apply the following simple relations of current and resistance: —

$$(1) \quad I = i_1 + i_2,$$

$$(2) \quad i_1 r_1 = i_2 r_2.$$

But $i_2 = \gamma a$, and $r_2 = 1100$, always.

$$\therefore 1100 \times 0.000000265 \times a = i_1 r_1 = i_2 r_2.$$

Here, r_1 being known, i_1 is determined, and from (1), I is found. The shunt resistance, r_1, was changed as the main resistance R was altered, so as to maintain the same deflection of the galvanometer.

For measuring the ohmic resistance of the voltameter,

Kohlrausch's method with induction coil and electrodynamometer was used.

The connections for this measurement are indicated in Fig. 2, in which B is the battery, C the commutator, I an induction coil, E an electrodynamometer (with key k), R a resistance box of the P.O. pattern, and V the voltameter.

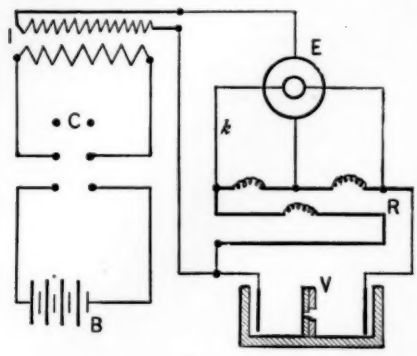

Fig. 2.

A solid iron core was used in the induction coil to avoid the great difference in the direct and inverse currents which exists when a wire core is used, and which results in a polarization of the voltameter. The P.O. box was used as a wheatstone bridge, of which the voltameter was one arm, and the movable coil of the electrodynamometer was connected across the branches of the bridge, the fixed coils being in series with the main circuit. Being thus used only as a galvanoscope, its constant need not be discussed; suffice it to say that the arrangement was sensitive to several decimals, though resistance was measured only to hundredths of an ohm.

The voltameter is simple, though its construction involves the only novelty in the apparatus. The voltameter first used was a glass vessel 18 cm. long, 6 cm. wide, 8 cm. deep, with a hard rubber partition sealed in with sealing-wax, in the middle. The opening in the vulcanite was 3 cm. wide and extended to within 2 cm. of the bottom. This frame for the partition was made by sealing two pieces of vulcanite together with a rim between of the same thickness as the glass plates bearing the metal partitions, which were slipped down into the groove thus formed. This was convenient, as the plates could be easily and quickly changed; but a quantitative test showed leakage around the edge of the glass plate of nearly 20 per cent of the conductivity when the plate was open, using solid and bored glass respectively; hence the results obtained with this voltameter are only relative, — not quantitatively correct.

This voltameter and its results would not be mentioned here but for the fact that I was so careless as to think that this tight-fitting glass would not allow sensible leakage under the circumstances, and to make a long series of measurements before testing the leakage quantitatively, and that, too, with some solutions which I have not had time to repeat.

The voltameter as finally adopted consists of a glass vessel, 20 cm. long, 12 cm. wide, 11 cm. deep. In the middle is fixed, by sealing-wax, a plate-glass partition, 3 mm. thick, with a hole in the center, 2 cm. in diameter. A smaller glass plate, with hole 1.5 cm. in diameter, is sealed over this opening, the metal partition being first sealed over the hole in the small glass. This gives two water-tight compartments, with no electrical communication except through the metal under experiment, which covers the hole in the glass. The end electrodes are of platinized platinum, 4 by 6 cm., and 0.1 mm. thick. With $CuSO_4$ solution, copper electrodes were used. Very thin plates of metal, even ordinary gold-leaf, were easily sealed over the hole in the small glass plate by laying the foil on smooth paper, carefully melting sealing-wax placed around the hole in the form of powder, and then cautiously picking the thin metal up with the melted wax. This accomplished, it is easy to seal the small glass plate over the opening in the partition. Each side of the voltameter could then be filled up to the lower edge of the opening; and, by carefully pouring the solution alternately in the two sides, little at a time, using a glass rod, the vessel could be filled above the gold-leaf, which showed surprising strength in being able to stand a difference of level of several millimeters.

For the voltameter in Fig. 1. we have the following relations: —

The voltameter included in the circuit and the partition open,

$$I=\frac{E-e}{R+r_3+\dfrac{1}{\dfrac{1}{r_1}+\dfrac{1}{r_2}}+v}$$

We are concerned only with the *change* in the auxiliary resistance, and not its absolute value, in order to make the current

the same when the partition is changed, and hence may simplify the case by representing the sum in the denominator by W; therefore, —

$$\left.\begin{array}{l}(1)\quad I=\dfrac{E-e}{W}, \text{ with partition open.}\\ (2)\quad I=\dfrac{E-e-x}{W-w}, \text{ with metal partition.}\end{array}\right\}\quad \therefore\ \frac{E-e}{W}=\frac{E-e-x}{W-w}$$

$$\therefore\ x=w\left(\frac{E-e}{W}\right)=Iw.$$

(*A*) $x=Iw=$ polarization on the partition.

$$(3)\quad I=\frac{E}{W+w_1-v}, \text{ with voltameter cut out of the circuit.}$$

$\therefore$ from (1) and (3),

(*B*) $e=I(w_1-v)=$ polarization on the end electrodes.

In every case the auxiliary resistance was so adjusted as to make the current as nearly as possible the same with partition in and partition out. This could not be done exactly, but was corrected by interpolation. We shall be mainly concerned with the polarization on the partition, and we see from (*A*) that this polarization expressed in volts is the simple product of current strength in amperes and the *change* of resistance necessary to keep the current constant when the partition is added that it was with partition open.

The same box of resistance was used for all purposes (in determining the "figure of merit" of the galvanometer, the resistance of the voltameter, and as rheostat to regulate the main and branch currents); hence we are not concerned with the question as to whether the units are true ohms.

Solutions used as Electrolytes.

With the old voltameter, relative values have been obtained for 30 % H_2SO_4, 5 % H_2SO_4, and very dilute H_2SO_4, such as to give voltameter resistance of about 20, 60, and 100 ohms. With

the new voltameter, quantitative measurements have been made with

30% H_2SO_4; Sp. Gr. = 1.22; v = 1.1 ohms.

$CuSO_4$; Sp. Gr. = 1.12; v = 24.5 ohms.

NaCl; Sp. Gr. = 1.12; v = 5.5 ohms.

Also some observations with

3% H_2SO_4; Sp. Gr. = 1.02,

KOH; Sp. Gr. = 1.11,

and *very* dilute sulphuric acid.

As partitions in the voltameter, platinum, gold, silver, and aluminum have been used, such as are described below. The thickness of the thick plates was measured with a micrometer gauge; that of the thin plates was calculated from their size, weight, and specific gravity. The plates marked S. & W. were from Sy and Wagner, of Berlin, and are supposed to be quite pure. Those marked M. are from F. Mueller, of Dresden, and are some pure, as indicated, others of the quality of the finest gold-leaf, *i.e.* 0.925 pure. It will be convenient in the tables to refer to these partitions by the *numbers*, and the following description will suffice once for all: —

THICKNESS OF PARTITIONS, EXPRESSED IN MILLIMETERS.

No.	Gold.		Platinum (pure).		Silver (S. & W., pure).	Aluminum (commercial).
0	S. & W., pure	0.25				
1	M., pure	0.0472	S. & W.	0.1	0.0023	0.4
2	M., $\frac{925}{1000}$	0.0241	S. & W.	0.002		0.00051
3	M., $\frac{925}{1000}$	0.00433	M.	0.000152		
4	M., $\frac{925}{1000}$	0.00183	S. & W.	0.0173		
5	M., $\frac{925}{1000}$	0.000586	S. & W.	0.00407		
6	M., $\frac{925}{1000}$	0.000382				
7	M., $\frac{925}{1000}$	0.000087				

The series of gold plates is fairly complete. They were beaten to order by Ferdinand Mueller in Dresden. Effort was made to

get a similar series of platinum, but as platinum foil for "silvering" seems to have fallen into disuse, I was unable to find any one prepared to make it for me. This is unfortunate, as platinum is

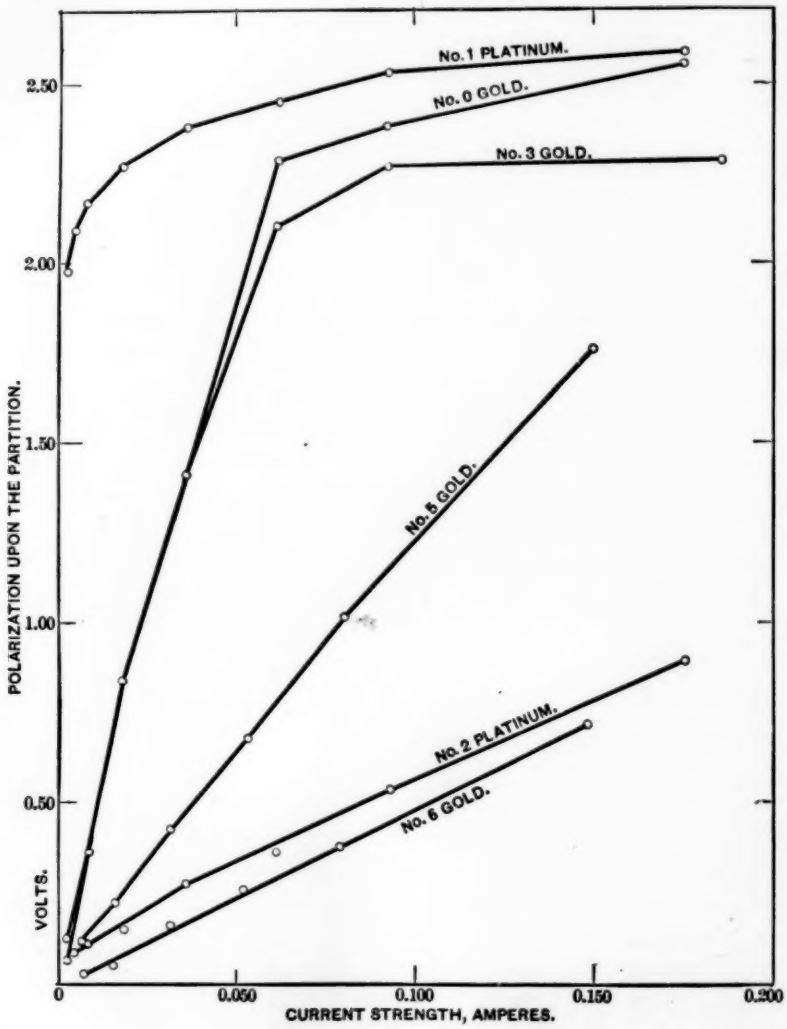

Fig. 3.

the only metal which seems to remain free from chemical action under a strong and long-continued electric current. However, as No. 2 and No. 3 of the platinum happen to fall below and between

the critical limits respectively, they serve as a very important check upon the results obtained with the more complete gold series, and show that these results are at least qualitatively correct. Below will be found reasons for believing them to be quantitatively correct.

In the tables which follow, I = current in amperes passing through the voltameter; x = polarization, in volts, on the metal partition; v = ohmic resistance of the voltameter, partition open.

Table I. was obtained with the old voltameter.

TABLE I.

H_2SO_4	V	I	Gold Plates.					
			No. 1.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.
30 %	1.6	0.1345	0.67	0.78	0.50	0.52	0.35	0.0
30 %	1.6	0.0665	0.33	0.35	0.23	0.24	0.16	0.0
30 %	1.6	0.0443	0.22	0.26	0.17	0.17	0.12	0.0
30 %	1.6	0.0222	0.12	0.14	0.10	0.10	0.05	0.0
5 %	5.7	0.78	1.42	1.65	1.19	0.98	0.70	0.04
5 %	5.7	0.0513	0.93	1.11	0.79	0.67	0.46	0.02
5 %	5.7	0.031	0.56	0.68	0.48	0.41	0.28	0.01
Very Dilute	101.7	0.0047	1.67	1.72	1.21	1.06	0.70	0.04
	101.7	0.0029	1.02	1.07	0.74	0.67	0.42	0.03

The results in Table II. were obtained with the new voltameter without leakage. They are shown graphically in Fig. 3. The readings were taken after waiting two minutes for the current to become steady when a new plate was inserted, or the resistance changed for a new current strength; and in case of the thicker plates where the time change in the polarization was more pronounced and continued longer, five to ten minutes was allowed between readings, or in each case until the galvanometer indicated that the current had become about constant. Later tests given in another table show that this time change of polarization, especially for thick plates, though at first rapid and then very slow, really continues some time.

TABLE II.

CURRENT ALTERNATELY DECREASING AND INCREASING.

30% H_2SO_4; v = 1.1 ohms.

I	0.175	0.093	0.061	0.037	0.018	0.009	0.004	0.002
No. 0 Au. (25 mm.)	[1] 2.83	2.37	2.03	1.28	0.67	0.33	0.17	0.09
	2.66	2.34	2.15	1.45	0.71	0.35	0.16	0.09
	[2] 2.66	2.39	2.19	1.42	0.73	0.38	0.18	0.11
	[3] 2.66	2.56	2.33	1.53	0.79	0.39	0.20	0.12
	2.38	2.25	2.15	1.15	0.55	0.33	0.19	0.12
No. 1 Au.	[4] 2.36	2.39	2.29	2.27	2.18	2.10	1.90	1.02
No. 1 Pt.[5]	2.52	2.48	2.42	2.39	2.28	2.17	2.08	1.98
	2.59	2.52	2.44	2.39	2.28	2.18	2.09	1.98
No. 2 Pt.[6]	0.89	0.53	0.36	0.26	0.15	0.108	0.085	0.07
	0.89	0.53	0.35	0.25	0.15	0.108	0.085	0.07
No. 1 Ag.[7]	0.87	0.46	0.42	0.26	0.20	0.12	0.09	0.08
	[8] 0.53	0.28	0.31	0.15	0.15	0.12	0.096	0.08

REMARKS. — [1] Profuse gas. [2] Without opening circuit. [3] Decreasing after circuit was closed 2.5 hours. [4] Very long between readings; gas. [5] Gas; negative side of partition gilded, the solution having been often used with gold plates. [6] No visible gas. Plate gilded. [7] No gas. [8] Oxidized and very irregular.

No. 1 Al. too much oxidized and too irregular to measure.

	No. 2 Pt.					No. 4 Pt. (very constant).		
	H_2SO_4 30%.	v = 1.1.	NaCl.	Sp. Gr. = 1.09.	v = 6.24.	NaCl.	Sp. Gr. = 1.12.	v = 5.5.
I	0.176	0.092	0.177	0.036	0.089	0.176	0.089	0.035
X	1.13	0.58	3.34	1.55	3.00	3.71	3.58	3.31

REMARKS. — With $CuSO_4$, Sp. Gr. = 1.12; $v = 24.5$; Cu. electrodes. No. 1 Pt. very constant and, for $I = 0.18$, $x = 2.19$. No. 7 Au., No. 3 Pt., and No. 2 Al., no polarization. No. 1 Ag. dissolved.

TABLE II. (*continued*).

30% H_2SO_4; v = 1.1 ohms.

No. 2 Au.	I	0.152	0.081	0.053	0.032	0.016	0.008	Long time readings; gas.	
	X	3.05	2.96	2.98	2.86	2.79	2.72		
No. 3 Au.[1]	I	0.184	0.093	0.061	0.037	0.019	0.009	0.004	0.002
	X	2.57 2.29	2.42 2.28	2.00 2.11	1.41 1.41	0.83 0.83	0.37 0.37	0.15 0.15	0.07 0.07
No. 5 Au.	I	0.150	0.080	0.053	0.032	0.016	0.008	No visible gas.	
	X	1.76 1.73	1.02 0.99	0.68 0.65	0.42 0.41	0.22 0.22	0.105 0.105		
No. 1 Pt.[2]	I	0.168	0.091	0.062	0.036	0.018	0.009	0.004	0.002
	X	2.87	2.72	2.65	2.55	2.39	2.23	2.07	1.99

REMARKS. — No. 7 gold, no gas: circuit closed 2.5 hours. $I = 0.15$; no polarization. No. Al. and No. 3 Pt., no gas; no polarization. [1] Gas developed. [2] Fresh solution, circuit closed 4 hours.

30% H_2SO_4; $v = 1.1$.				3% H_2SO_4; $r = 6.3$.[3]			
No. 6 Au.				No. 1 Au.[1]		No. 2 Au.[2]	
I	X	X		I	X	I	X
0.149	0.71	0.71		0.174	2.78	0.156	2.67
0.079	0.38	0.38		0.089	2.66	0.091	2.59
0.052	0.25	0.25		0.060	2.65	0.061	2.61
0.032	0.15	0.15		0.036	2.61	0.037	2.56
0.016	0.06	0.06		0.018	2.55	0.018	2.49
0.008	0.03	0.03		0.009	2.49	0.009	2.43
No visible gas.				0.004	2.38	0.004	2.43
				0.002	2.30	0.002	2.28

REMARKS. — [1] Long-time readings; gas; gold oxidized. [2] Long-time readings; gas. [3] A trial made with No. 7 gold; circuit closed 2.5 hours; no gas; showed X too small to measure.

TABLE III.

CHANGE OF X WITH TIME. VALUES FOR DIRECT (a) AND REVERSED (b) CURRENT.

$I = 0.175$; H_2SO_4, 30%; $v = 1.1$ ohms.

Time.	End electrodes.		No. 1 Pt.[1]		No. 2 Pt.[2]		No. 0 Au.[3]		No. 4 Au.[4]
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*
1′	1.73	1.44	1.91	—	0.97	0.96	2.14	1.94	2.37
3′	—	—	2.08	2.01	1.02	1.02	2.25	—	2.43
5′	1.77	1.76	2.14	2.13	—	1.06	—	2.06	2.49
10′	1.78	1.77	2.21	2.15	1.07	—	2.34	2.14	2.55
20′	1.79	1.78	2.24	2.17	1.09	1.11	2.45	2.17	2.63
30′	1.80	—	2.30	—	1.10	1.12	2.48	2.19	2.66
45′	1.81	1.81	2.33	—	1.11	1.13	—	2.25	2.70
60′	—	—	2.35	—	—	—	—	2.27	2.54
75′	1.84	—	2.36	2.35	—	—	—	2.28	—
100′	1.84	1.84	—	—	—	—	2.53	—	2.41
150′	—	—	—	—	—	—	—	—	2.27
220′	—	—	—	2.46	—	—	2.55	—	0.00

REMARKS. — [1] Slightly gilded. [2] No visible gas. [3] Oxidized; gas. [4] Gas, till oxidation had reduced the plate to a thin film. The oxide then fell off, and polarization ceased.

Time.	No. 1 Pt.[1]		No. 5 Pt.[2]		No. 2 Pt.[3]	No. 4 Pt.
	a	*b*	*a*	*b*	*a*	*b*
1′	2.17	1.98	2.37	1.99	2.97	3.51
3′	2.34	2.10	2.45	2.08	—	3.56
5′	2.43	2.16	2.53	2.12	3.34	3.67
10′	2.53	2.30	2.65	2.24	3.34	3.71
20′	2.68	2.42	2.74	—	3.34	3.72
30′	—	2.53	2.83	—		
45′	2.85	2.73	—	2.59		
60′	—	—	—	2.63	Gas.	Gas.
75′	—	—	—	2.67		
100′	2.92	—	2.90	—		
150′	—	2.87	—	—		
220′	—	—	—	2.68		

REMARKS. — [1] Fresh solution; 30 % H_2SO_4. [2] NaCl. (Sp. Gr. 1.09), $v = 6.24$. [3] NaCl. (Sp. Gr. 1.12), $v = 5.5$.

No. 3 Pt., No. 7 Au., and No. 2 Al. showed no polarization.

The following is a sample page of my note-book, showing how the observations were recorded and the tables derived: —

NO. 7 GOLD IN 30% H_2SO_4.

Zero of scale.	Scale reading.	Deflection, a.	Shunt, r_1.	Auxiliary resistance, R.	Branch resistance, r_2.	Sensibility, for 1 ohm, σ.	Change of resistance, w.	Polarization, $\sigma w = x$.
337.5	940.0	—	—	—	—	—	—	—
336.0	939.0	603.0	1	28	1100	20.0	0.1	0.014
338.0	981.0	—	—	—	—	—	—	—
336.0	981.0	644.0	2	55	1100	12.0	0.02	0.016
338.0	974.0	—	—	—	—	—	—	—
337.0	973.0	636.0	3	85	1100	7.5	0.0	0.0
338.0	976.0	—	—	—	—	—	—	—
337.0	977.0	639.0	5	143	1100	5.0	0.0	0.0
338.0	984.0	—	—	—	—	—	—	—
337.0	983.5	646.0	10	287	1100	2.5	0.2	0.003
337.0	958.5	—	—	—	—	—	—	—
337.0	958.5	621.0	20	597	1100	1.0	1.0	0.008

The No. 7 gold removed with a glass rod, not opening circuit.

						Current i.
336.0	940.5	—	—	—	—	
336.0	942.0	605.0	1	28	1100	0.1492
336.0	979.3	—	—	—	—	—
336.0	981.3	644.3	2	55	1100	0.0795
336.0	972.0	—	—	—	—	—
336.0	972.0	636.0	3	85	1100	0.0524
336.5	975.0	—	—	—	—	—
336.0	976.0	639.0	5	143	1100	0.0316
336.5	981.5	—	—	—	—	—
336.0	982.0	645.0	10	287	1100	0.0161
336.0	956.5	—	—	—	—	—
336.0	956.5	620.0	20	597	1100	0.0078

The two readings in each case are for decreasing and increasing current respectively.

Then, $i_2 = \gamma a \quad = 0.000000224 \times 605 = 0.0001355.$

$i_1 r_1 = i_2 r_2 \quad = 0.0001355 \times 1100 = 0.14905 = i_1$, since $r_1 = 1$.

$I = i_1 + i_2 = 0.1492$ amperes.

$w = R - R' =$ two scale divisions $= \frac{2}{20} = 0.1$

($20 = \sigma =$ scale divisions for changing R one ohm).

$I w = x = 0.014$ volt.

In this manner, from such a table in the note-book, one line in Table II. was obtained. The sample page of my notes for No. 7 gold was selected to illustrate the method of observation and reduction, because it also serves as a fair sample of many efforts to measure quantitatively the polarization on gold-leaf in good-conducting (30 %) H_2SO_4. One has only to look at the time variation of the polarization on the end electrodes to be able to account for such slight variations from zero as occur here (see Table III.). Having become satisfied from many such series of observations that there was no measurable polarization on gold-, aluminum-, and platinum-foil for the currents used, I then adopted an efficient method of testing them for polarization in various solutions, viz. to allow the strongest current to flow through the plate long enough to become constant, and then, without opening the circuit, to remove the metal partition with a glass rod and simply observe for a change of deflection of the galvanometer. On this method of observation is based the statement under the tables, that for these thinnest partitions there is no polarization for the currents used. The qualitative results of Table I., with the old voltameter, seem to indicate pretty clearly a small polarization on No. 7 gold in very dilute (bad-conducting) acid. A preliminary test with the new voltameter of water containing only a few drops of acid, using gold-leaf as a partition, showed sufficient polarization to develop visible gas.

TABLE IV.

RELATION OF POLARIZATION TO THICKNESS; 30 % H_2SO_4; GOLD PLATES.

Current (I).	No. 6, 0.00038 mm.	No. 5, 0.00059 mm.	No. 3, 0.00433 mm.	Ratio, $d^2 : x$.
	x	x	x	
0.01	0.04 volts	0.9 volts	0.40 volts	441 : 484
0.02	0.09	0.26	0.77	1274 : 1081
0.03	0.13	0.39	1.13	1911 : 1694
0.04	0.19	0.50	1.48	2450 : 2299
0.05	0.28	0.76	2.02	3724 : 3388
0.10	0.47	1.23	2.35	6027 : 5681
0.15	0.71	1.76	2.35	8624 : 8591

From this table it seems that for a given current strength the polarization is fairly proportional to the square of the thickness of the partition for plates near the lower critical thickness (see Fig. 4). The last column of Table IV. shows this ratio as worked out for No. 5 and No. 6 gold.

We may now briefly summarize the experimental observations.

(1) The polarization on a gold-leaf partition in good-conducting H_2SO_4 is zero, or too small to detect with our apparatus, for the range of current used.

(2) The "critical thickness" in good-conducting solutions of H_2SO_4, $CuSO_4$, and NaCl is *greater* than 0.00009 mm. for gold; 0.00015 mm. for platinum; and 0.0005 mm. for aluminum, under the above conditions. It is *less* than 0.0004 mm. for gold; 0.002 mm. for platinum; and 0.002 for silver.

(3) The "upper critical limit" of thickness under these conditions seems to be about 0.004 mm., rather less than for No. 3 gold.

(4) Tables I., II., and III. all point to the conclusion that between the "critical limits" of thickness the polarization for a given current increases with the thickness.

(5) Table II., showing relation of polarization to current, expresses two interesting facts: (*a*) that the polarization on "thick" plates is about the same, in this voltameter, for all currents be-

tween 0.2 ampere and, say, 0.01 ampere, provided time enough be allowed in each case for the current to become constant; *i.e.* between the upper limit of current at which the development of gas is so profuse as by mechanical obstruction and irregular escape to interfere, and the lower limit, at which the formation of gas is

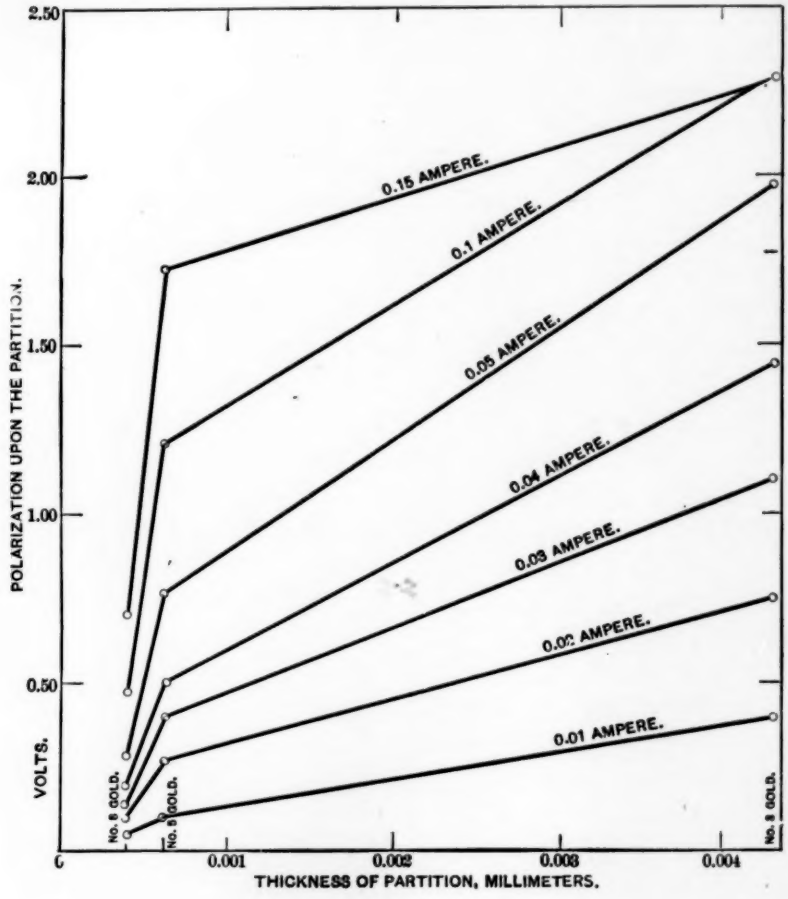

Fig. 4.

no faster than it can be dissipated. (*b*) Quite different is the case for "thin" plates, where, within the limits of current and thickness prescribed, the polarization is dependent upon the current and gives for each thickness a different curve, or rather straight line, for they are all straight lines converging to the origin, and differ-

ing only in *slope*. The current strength at which the polarization on very thin plates would reach a maximum is far above that used, being, perhaps, expressed in amperes instead of tenths and hundredths.

By *thick* plates are defined those above the "upper critical limit"; by *thin* plates, those below this limit of thickness.

(6) Inspection of Table III., which gives the time change of the polarization, will show a similar distinction between "thick" plates and "thin" plates, as was noted in the last paragraph; viz. that for thick plates the change is considerable and continues slowly for hours; for thin plates, the change of polarization with time is both less pronounced and extends over much less time.

(7) It was noted, especially in the case of $CuSO_4$ as electrolyte, that there was polarization on gold-leaf if the gold exposed contact with the solution some distance beyond the edge of the hole in the glass plate to which it was sealed; thus in $CuSO_4$, for the stronger currents used, there was a symmetrical deposit of copper decreasing in thickness from the outside toward the center, and vanishing at a small distance from the edge of the hole, this distance being less the stronger the current. If only one corner was left exposed, the copper was deposited there. This phenomenon was further tested by bending a thick strip of aluminum 4 cm. long into the shape of a narrow U and simply hanging this U in the *open* hole of the glass partition in $CuSO_4$ and closing the circuit on the voltameter; the two ends of the metal strip being thus in contact with the $CuSO_4$ on opposite sides of the glass two cm. from the edge of the opening, there was decided deposit of copper on one end and escape of oxygen from the other end.

(8) In $CuSO_4$, all the plates except those below the critical thickness were destroyed by oxidation. No. 1 silver was destroyed in less than one minute. Of course gold and silver above the critical thickness could not be used in NaCl because of chemical action, though the thinnest plates were quite unaffected. Only the No. 7 gold was tested in KOH, as it dissolved the sealing-wax.

(9) Thick plates of gold were strongly oxidized in H_2SO_4, especially with strong currents. Thin gold plates were appar-

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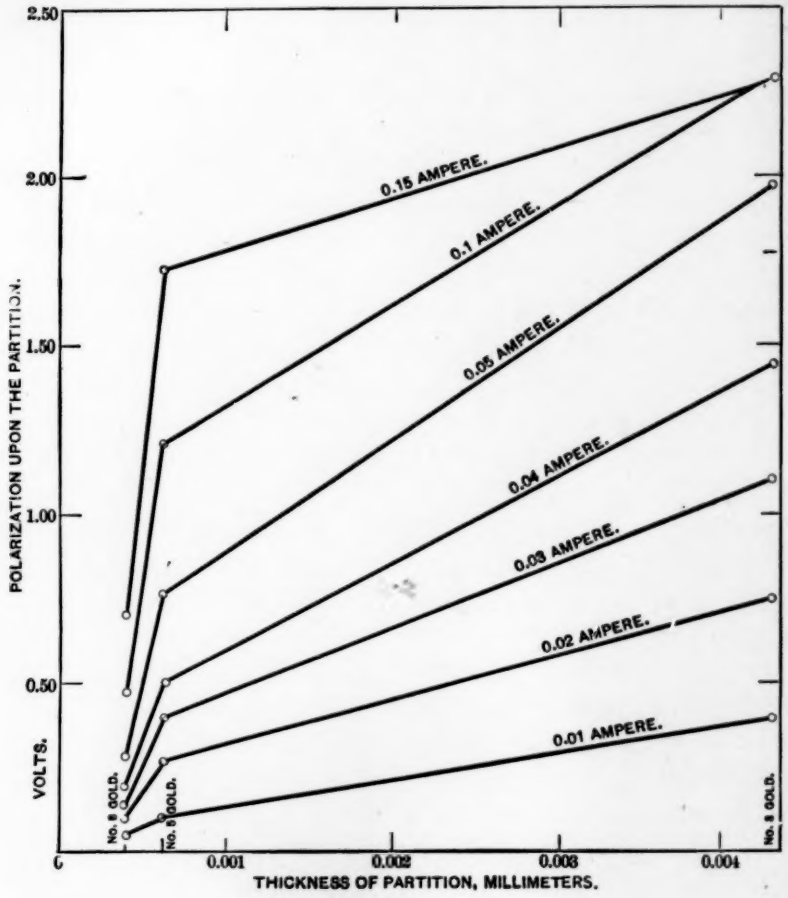

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ently only oxidized under action of strong or long-continued currents. Compare Tables II. and III. Silver was even more easily oxidized than gold. Aluminum was so intensely oxidized by the current that no satisfactory measurements could be made for this metal, though the thin foil was unaffected.

(10) With H_2SO_4 as electrolyte, after a thick plate of pure gold had been used as partition for the time change of Table III., the end cathode was found to be gilded. A thick platinum plate being then substituted for the gold in the same solution for the results of No. 1 platinum in Table III., the platinum partition was found, on removal, to be gilded. The polarization for No. 1 platinum in this case was somewhat less than for the same platinum after both it and the end electrodes were thoroughly cleansed, the electrodes re-platinized, and fresh solution made.

(11) The polarization in $CuSO_4$, using copper electrodes, reached a maximum almost immediately, and remained very constant. The maximum polarization for thick platinum in $CuSO_4$ was hardly 75 per cent that for the same in H_2SO_4. In NaCl the polarization became constant very quickly also, but its value was decidedly greater, especially on thin plates, than in H_2SO_4; though the same distinctive behavior of thick and thin plates was observed.

(12) In H_2SO_4 of different concentrations, the maximum polarization for a partition was of the same order of magnitude; but its value for very weak currents was decidedly greater in weak solutions than for the same current in stronger solutions up to 30 per cent. This shows itself especially with thin plates, and also in the shorter time required for thick plates to reach a maximum polarization with weak currents. The greater change in temperature and the greater change in concentration of weak solutions may account for this.

For currents between 0.1 and 0.2 ampere, the polarization on the end electrodes was 1.84 for H_2SO_4; 1.98 for NaCl; and 0.00 for $CuSO_4$, with copper electrodes; though if the current density was too great, or the time too long, the anode would oxidize and become irregular.

C. Fromme, in a paper, "Ueber das Maximum der galvanischen

Polarisation von Platinelektroden in Schwefelsaeure" (*Annalen d. Physik u. Chemie*, Band XXXIII., S. 80–126), states that the maximum polarization varies both with the concentration and the relative size of the electrodes, the extreme limits being given as 1.45 to 4.31 volts—the minimum polarization coinciding with maximum conductivity. His method for measuring polarization was somewhat similar to that used in this work. As bearing upon "the change of polarization with time," I would refer especially to the investigation of Dr. E. Root upon this subject, discussed by Professor von Helmholtz.[1] These experiments by Dr. Root seem to prove clearly that the liberated ions penetrate deeply into the electrode, even when liberated upon but one side of it, as in his experiment. I take great pleasure in expressing here my thanks and deep obligation to Professor A. Kundt and Dr. L. Arons for their kind sympathy and direction in this work.

[1] Wissenschaftliche Abhandlungen, Bd. I., p. 835.

PHYSICAL LABORATORY, UNIVERSITY OF BERLIN,
August, 1892.

SOME MEASUREMENTS OF THE TEMPERATURE VARIATION IN THE ELECTRICAL RESISTANCE OF A SAMPLE OF COPPER.[1]

BY A. E. KENNELLY AND REGINALD A. FESSENDEN.

I.

PRECISION in the determination of the temperature variation of resistance in copper is important not only to electrical science, but also to its applications. Our estimate of the temperature of remote or inaccessible positions, as, for example, the ocean bed on which a submarine cable lies stretched, or the interior layers of a dynamo armature winding, are often directly dependent for their accuracy upon the completeness of our knowledge of this temperature coefficient.

Electrical text-books, in stating the temperature coefficients of copper, usually quote the results of Dr. Matthiessen, or of Dr. Siemens, or both. The results of these two authorities are discordant.

Within the range of chamber temperatures, say from 0° C. to 35° C., the difference between these results is practically of little importance. Taking, however, the resistivity of copper at zero centigrade as unity, its resistivity at 100° C. is 1.422 by Matthiessen's observations, and 1.388 by those of Siemens, a variation of nearly $2\frac{1}{2}$ per cent, while above 100° C., or below 0° C., this discrepancy increases rapidly.

First in order of date are the elaborate researches of Matthiessen (and of his collaborator Von Bose), appearing in the *Philosophical Magazine* for February, 1857, and February, 1861, also in the *Philosophical Transactions* for 1858, 1860, 1862, and 1864, the most important series from our present standpoint being those for 1862. The wires tested were varnished with shellac,

[1] Read at the International Electrical Congress, Chicago.

and immersed in a bath of oil whose temperature was raised by the application of Bunsen burners, and read off by an immersed thermometer. Readings were taken both in ascending and descending series of temperature, and observations are adduced in support of the statements that the application of varnish did not affect the results, and that the observations on a wire heated in a bath of oil were sensibly the same as when the heating took place in air. Matthiessen took six copper wires, all from the same electrolytic source, three annealed and three hard-drawn. Six observations are given of the resistances of each between 0° and 100° C. Having ascertained that all 36 observations accorded very fairly with a parabolic relation between conductivity and temperature, the parabola of closest conformity computed by the method of least squares was $\lambda = 1 - at + bt^2$, or numerically $\lambda = 1 - 0.0038701\, t + 0.000009009\, t^2$, λ being the conductivity at temperature $t°$ C. From this equation, the resistivity (the reciprocal of λ), retaining the terms necessary for accuracy in the fifth digit, at the limit of 100° C. becomes,

$$\rho = 1 + 3.8701\, t \times 10^{-3} + 5.968\, t^2 \times 10^{-6} - 1.177\, t^3 \times 10^{-8} - 9.93\, t^4 \times 10^{-11} - 2.769\, t^5 \times 10^{-13}.$$

The graph of this equation, taking values of ρ as vertical ordinates from a horizontal axis of temperatures as abscissæ, yields a curve bending upwards, so that the temperature variation increases with the temperature, the increase in resistance per degree centigrade being at 0° C. 0.387 per cent, and at 100° C. 0.50 per cent of the resistivity at zero C. Matthiessen points out that this bending upwards of the curve is distinctly indicated by his results, and that no straight line can represent them. Not only the 36 observations on copper wires, but more than 200 quoted observations on other metals, all point to a temperature coefficient augmenting with temperature, and negative the supposition of a simple linear relationship between the variables.

Dr. Siemens' researches formed the subject of his Bakerian lecture in 1871. They were undertaken with the object of obtaining a practically reliable scale for the electropyrometer which bears his name, rather than for the direct purposes of scientific

research. After pointing out that Matthiessen's formula can on its own evidence be only fairly applicable between the limits of 0° and 100° C., Dr. Siemens proceeds to advance some interesting, although arbitrary, hypotheses for the law of temperature variation in metallic resistances, and then shows that his experimental observations on copper and four other metals are capable of close representation by the empirical formula so obtained. These observations were made on wires heated in air, and also in oil, up to 350° C. with mercury thermometers, and in one series up to 850° C. with a platinum ball pyrometer, an instrument whose indications assumed a constant specific heat in the platinum ball throughout the range of temperature employed.

Dr. Siemens' formula for copper is $\rho = 0.026577\sqrt{T} + 0.0031443\,T - 0.29751$, where ρ is the ratio of the resistivity at any absolute temperature, T, to that at zero centigrade, or $T = 273°$. For 100° C., or $T = 383°$, $\rho = 1.3885$, and the rate of increase of resistivity is at 0° C. 0.394 per cent, and at 100° C. 0.383 per cent of the resistivity at zero C. The graph of the equation is a curve bending slowly downwards towards the axis of temperatures, and the temperature variation diminishes as the temperature rises. All the 170 observations recorded in the paper indicate that the curve bends downward, while all the 250 observations in Matthiessen's 1862 paper make the curve bend upwards. The discrepancy between these two series of results becomes very noticeable between 70° and 100° C.

Professors Dewar and Fleming have published in the *Philosophical Magazine* for October, 1892, a number of observations on the resistivity of metals and alloys at temperatures between −200° C. and +100° C., one series for copper being included. The resistivity of the copper wire is stated to have been 1353 C. G. S. U. at 0.7° C., equivalent to 1349 at 0° C.; and since Matthiessen's standard is 1594 at zero C., this represents a conductivity 18 per cent higher than Matthiessen's standard. Aside, however, from this remarkable and perhaps debatable statement, the graph of the observed values of resistance with respect to temperature is very nearly a straight line throughout the whole range, the resistivity at 100° C. being 1.424 times greater than that at 0° C., and

the temperature coefficient being approximately 0.424 per cent per degree centigrade for all temperatures between $-200°$ and $+100°$ C.

Messrs. Cailletet and Bouty, in the *Comptes Rendus* for 1885, give an observed temperature coefficient for copper of 0.418 per cent per degree C., expressed by $\rho_t = \rho_0 (1 + 0.00418\, t)$ between zero and $-58°$ C., and 0.425 per cent from $-69°$ to 123° C., $\rho_t = \rho_0 (1 + 0.00425\, t)$.

In Poggendorf's *Annalen* for June, 1858, Herr Arndtsen quotes a uniform temperature coefficient of 0.369 per cent per degree from zero to 200° C. He gives, however, one series of observed resistance with a copper wire (containing 0.15 per cent of iron) between 0° and 100° C., showing a linear relation, or a temperature coefficient of 0.394 per cent per degree C., $\rho_t = \rho_0 (1 + 0.00394\, t)$, and he points out that the divergences from the straight line are within the limits of the observation error.

In view of the discrepancies existing between these best known measurements of the temperature coefficient of copper, Arndtsen, Cailletet, and Bouty giving results practically represented by straight lines, Siemens' results with the line bending distinctly downward and Matthiessen's results with the line bending as distinctly upward, the writers of this paper made a number of measurements in the spring of 1890 upon a sample of copper wire. These measurements were made with great care, and repeated until similar results were obtained in successive series. The wire tested was sealed within the bulb of an air thermometer, so that there could be no appreciable variation between the temperature of the wire itself and the temperature indicated by the pressure of the air in the bulb it occupied. The final results, after full corrections for expansion of the bulb, etc., indicate a linear relation between the resistance and temperature of the wire between the limits of 20° C. and 250° C., represented by the equation $\rho_t = \rho_0 (1 + 0.00406\, t)$, indicating a uniform temperature coefficient of 0.406 per cent per degree C. throughout the range, the maximum observed being 0.4097 per cent, and the minimum 0.399 per cent at any point. The details of these measurements are here submitted in the form of an appendix, not only in support of the

statements made concerning them, but also because the experimental arrangements of apparatus finally successful were the outcome of a series of experimental failures, and it is believed that the details of construction may be of service to those who desire to adopt the same method of measurement.

Concerning the conclusions that may be drawn, we feel only justified in saying that good commercial copper can be found in which a linear relationship holds between resistance and temperature between 20° C. and 250° C., and within the range of small observation errors. It is, of course, possible that in different samples of wire the temperature coefficient may increase or diminish with the temperature. In other words, the second differential coefficient of resistance with respect to temperature may perhaps in some samples be either positive or negative, but it seems desirable that fresh measurements should be made, and evidence collected to settle this point, and we submit the view that the best experimental means of measuring the temperature, and to ensure the coincidence between the measured temperature and that of the tested wire, is to enclose the latter in the bulb of an air thermometer in the manner here described.

II.

General Outline of Apparatus.

Within the cylindrical glass tube of an air thermometer was enclosed about 240 cm. of fine copper wire. Short platinum wires, sealed into the glass bulb, brought this copper wire into communication with apparatus for measuring its resistance. The bulb rested in an oil bath heated electrically, and the height of a mercury column required to balance the pressure of the internal air was measured by cathetometer, at the moment that the resistance of the copper wire was noted. The bulb was thus operated as an air thermometer at constant volume, and corrections were applied to the expansion of the glass walls of the bulb, and for the variation of barometric pressure during the period of observations; also electrically for the resistance of the leads up to and including the platinum seals.

Thermometer Bulbs and Contents.

A vertical section of the thermometer bulb and its accessories is shown to approximately one-sixth true scale in Fig. 1. *AB* is the cylindrical glass bulb 15 cm. long, and 3.15 cm. external, 2.85 cm. internal diameter. The capacity of the chamber so enclosed was approximately 75 c.c. Three separate platinum wires, 2 cm. long and 0.048 cm. in diameter, were sealed in at *D*, and welded with three exterior copper wires, *E*, *F*, and *G*, forming the leads to the apparatus. The central wire was also welded within the bulb to a copper wire, 10 cm. long and 0.08 cm. in diameter, and the seal supported this wire axially along the bulb to its termination at *H*.

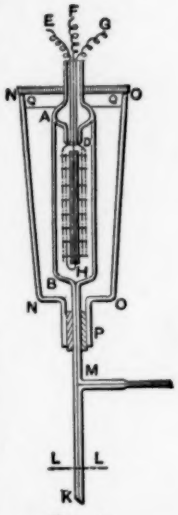

Fig. 1.

This copper wire *DH* was entirely covered by a glass tube, 10 cm. long and 0.25 cm. in external diameter, closely threaded, on which were beads or short cylinders cut from glass tubing, each bead being 1 cm. long, 0.28 cm. internal and 0.4 cm. external diameter. The beads served as sleeves or washers to clamp between them at their junctions circular disks of mica, 2.15 cm. in diameter and 0.02 cm. thick, with a hole in the centre, 0.25 cm. in diameter. Two circles of holes were drilled concentrically around this disk, each circle having fifteen holes. The diameters of these circles were 1.0 cm. and 1.65 cm. respectively. A plan view of a mica disk is shown in Fig. 2, to full scale.

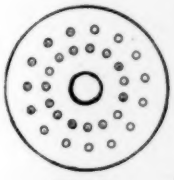
Fig. 2.

The copper wire tested was of good commercial quality, 0.002″ (0.0051 cm.) in diameter, and double silk covered. The silken covering was dissolved off with hot caustic soda, diluted so as not to oxidize the wire, and the bare wire threaded up and down through the mica disk, and parallel to the axis of the bulb; first filling up the inner cylinder of holes, and then the outer. The inside end was soldered to platinum wire, No. 1, connected with the lead *E*; the final exterior end soldered to platinum

wire No. 2, from lead G; and the junction or midway point connecting the inner and outer cylinders was connected to the copper wire at H, which communicated with lead F. By this means two separate loops of wire of nearly equal length were provided within the bulb, arranged in two cylinders, one within the other. The outer cylinder between leads F and G had a diameter of 1.65 cm.; the inner, between E and F, the diameter of 1.0 cm. The object of this arrangement was to furnish a check by duplicate, upon the observed resistance of the tested wire, and also to ascertain what difference in temperature, if any, existed between the air at radius 0.5 cm. and the air at radius 0.8 cm. from the axis of the bulb, the source of heat being entirely external. Had the mean temperature of the inner and outer cylinders differed at any time in virtue of gradient of temperature within the bulb, by one-tenth of one degree centigrade, it would have been within the range of observation; and had it amounted to one-fifth of a degree, it could not have escaped detection. No appreciable difference was at any time discovered, the increase of resistance in the two cylinders being always proportionally coincident, so that finally the two loops were combined into one for facility in observing, and only divided for an occasional check. The diffusion and convection of the air within the bulb must have been sufficiently rapid to practically equalize the temperature within the air space. The course of the wire within the bulb is indicated by the dotted lines in Fig. 1.

The bulb communicated with the mercury through a glass tube DK, round which a hair, secured 15.2 cm. below the bulb at LL, formed the fiducial mark. The diameter of this tube was 0.6 cm. externally and 0.1 cm. internally, and the volume of its bore from bulb to fiducial mark, including the offset tube at M, was 0.3 c.c. or $\frac{1}{250}$ of the volume of the bulb.

The bulb was held vertically upon the axis of a glass percolator, $NNOO$, the lower tube passing through a rubber stopper at P. The space between the bulb and walls of the percolator was filled with boiled linseed oil up to the level QQ, and a cylindrical grid of platinoid wire, not shown in the figure, was immersed in the oil. A steady current of from 2 to 3 amperes through

this platinoid wire of 16 ohms resistance served to raise the temperature of the oil and immersed bulb at a convenient rate. A disk of asbestos cloth, *NO*, rested as a cover upon the percolator, and more of the same material was wrapped around the exterior surface *NNOO*, in order to impede the escape of heat from the chamber.

When the apparatus was in position, a vertical wooden board, rising above a wooden trough set to catch any mercury that might escape, supported a long vertical tube in front of the cathetometer. A bottle of mercury and an equilibrating bottle of sand were supported by a cord running over pulleys fixed into the ceiling. Lowering the sand bottle raised the bottle of mercury and the attached rubber tube, bringing the level of the mercury in the index tube (allowing for capillarity) up to the same elevation.

Electrical Measuring Instruments. — The resistance of each cylindrical loop of wire within the bulb was about 10 ohms at the normal or initial temperature, in the vicinity of 20° C., making 20 ohms in all, and at the highest temperature reached in the measurements, these resistances doubled, so that the total range of observed change in resistance amounted to 10 ohms in each loop, or 20 when the loops were in series.

In the first trial, the resistances were measured by Wheatstone's bridge. This method was found to be unsatisfactory both in respect to swiftness and precision. In swiftness because the readjustment of the balance required some seconds to effect, and during that time the temperature of the wire might have altered; and in precision, since the resistance of the leads had to be subtracted, and these were likely to vary appreciably with the temperature of the room.

Later, two differential galvanometers were employed. One balanced the two loops within the bulb against each other to detect variations of temperature within the bulb, and the other compared the resistance of both loops in series against a fixed standard in platinoid wire (30 ohms).

Finally, the first galvanometer fell into disuse, since no variation could be detected between the resistances of the two loops, and measurements were confined to the second differential galva-

nometer, with one wheatstone bridge reading as a check at the outset, and another at the culminating temperature of the series.

The differential galvanometer method is very convenient for such measurement. It enables the variations of the tested resistance to be constantly watched, and balance can be quickly readjusted with a dead-beat instrument by rheostat thrown into the circuit of preponderating influence.

The main circuit consisted of the bulb with its two loops in series, a standard resistance of 30 ohms in platinoid, and an additional resistance of 50 ohms in a rheostat. A single Edison-Lalande cell delivered a steady current of from 6 to 7 milliamperes through this circuit. The two coils of the differential galvanometer had about 2700 ohms each; one was connected to the terminals of the standard 30 ohms, and the other to the terminals of the bulb. A change of resistance in circuit of either coil, amounting to 1 ohm, could be plainly observed on the scale.

Modus Operandi. — The bulb was repeatedly exhausted through its attached tube, then heated to 200° C. under a vacuum for an hour, to expel all moisture, and finally filled with dried air. It was then tightly connected with the mercury apparatus and index tube by double rubber pipes well jointed. The offset tube was opened through a chamber containing calcium chloride so as to acquire internally the pressure of the air, which was noted by mercurial barometer. The level of the mercury was raised at the same time to the fiducial mark, the temperature of the oil bath around the bulb observed, and the resistance of the enclosed copper wire measured. The temperature of the air close to the index tube was also taken. The offset tube was then sealed off with a blow-pipe, and the circuit of the platinoid grid in the oil bath closed. The level of the mercury was then raised in the index tube about 3.5 cm. to cathetometer observation, by lifting the mercury bottle through that distance, driving mercury into the bulb tube above the fiducial mark. The increasing temperature and pressure of the air within the bulb slowly forced the mercury in this column back to the fiducial mark, leaving the index elevation practically unaltered. At the moment that the mercury crossed the fiducial mark, the resistance for balance at the differential galvanometer

was noted. The level of the mercury in bottle and index tube would then be raised again another 3.5 cm., the mercury column elevated above the fiducial mark, the cathetometer reading taken, and the resistance balance when the mercury again crossed the line. This process was repeated step by step until the maximum temperature was reached. Meanwhile readings were kept of the barometer pressure in the room, and the temperature of the air by the side of the index tube.

No appreciable time lag existed in the bulb, owing to its small thermal capacity. After the highest desired temperature had been attained in a series, the differential galvanometer would indicate a lowering in the resistance of the copper wire, within ten seconds of the interruption of the heating current. The reduction in temperature could be detected electrically ten or fifteen seconds before the mercury could be observed to retreat. This lag in the mercury was traced, principally, at least, to the influence of fluid friction in the narrow tube. Tapping this tube with the finger was found to accelerate the mercurial movement. Later, the bulb tube whose internal diameter was 1 mm., in order to have as little volume of unheated air-space as possible, was welded into one of larger caliber (0.2 cm.) just above the fiducial mark, increasing volume of air-space outside the bulb to 0.4 c.c., but materially diminishing the fluid friction, so that tapping the tube was scarcely necessary.

A similar series of cathetometer and resistance readings was obtained as the oil bath and bulb cooled down. An entire set of observations generally lasted four hours.

The mercury employed was filtered and kept clean. The internal diameter of the index tube was 0.6 cm., but as its capillarity error entered equally into all the readings, no correction was required on this account.

The coefficient of expansion of the glass forming the bulb was measured by taking two globes blown from the same tubing as the bulb, drawing out their necks to a fine bore, filling them with a measured mass of mercury, at normal temperature, heating them up to their necks in mercury over a sand bath to 157° C. till they ceased to overflow, and the mass of mercury remaining was observed after cooling down.

The mean cubical expansion of the glass was

$$3\beta = (2800 \pm 113) \times 10^{-8},$$

and this value was assumed in all voluminal corrections.

Results. — The first four series of observations were rejected. When computed and plotted, with ordinates of resistance to abscissas of temperature, they showed curves bending slightly upwards, after the manner of Matthiessen's, but the descending curve was distinctly below the ascending branch, so that the diagram appeared to form a loop as though the wire had a lower resistance for a given temperature when cooling than when heating. The cause of this error is not known, but may have been due to fluid friction of the mercury in the bulb tube. With each successive series the curvature of the line diminished, the ascending and descending branches approaching one another. The fifth series was considered to be satisfactory. Its graph is practically a straight line with a slight divergence between upward and downward branches. The reduced observations are given in the accompanying

TABLE I.

	Temperature °C. by air thermometer.	Linear coefficient per °C.	Weighted mean.	Discrepancy.
	29.8	0.004037	0.004059	0.000022
	67.0	0.004076		0.000017
	79.8	0.004066		0.000007
	92.9	0.004085		0.000026
	104.7	0.004063		0.000004
	113.0	0.004055		− 0.000004
	131.4	0.004062		0.000003
	143.0	0.004058		− 0.000001
	155.0	0.004031		0.000022
	168.6	0.004037		0.000023
	181.7	0.004110		0.000051
Maximum	196.2	0.004084		0.000025
	169.0	0.004062		0.000003
	135.3	0.003999		− 0.000060
	123.6	0.003995		− 0.000064
	108.0	0.004010		− 0.000049
	92.0	0.004017		− 0.000042

The sixth series appeared to be the most reliable. Its graph is also practically a straight line up to the maximum temperature of 255 C. with no appreciable deviation between the ascending and descending branches, the latter being carried in this instance no lower than 207° C. The reduced observations referred to linear coefficients are given in the following

TABLE II.

	Temperature of copper wire in °C.	Linear coefficient of increase per degree.	Weighted mean.	Discrepancy.
	27.8	0.004007	0.004065	− 0.000058
	42.64	0.003984		− 0.000081
	56.55	0.004038		− 0.000027
	72.25	0.004027		− 0.000038
	87.11	0.004063		− 0.000002
	105.07	0.004172		0.000107
	123.99	0.004080		0.000015
	139.48	0.004141		0.000076
	154.17	0.004143		0.000078
	169.94	0.004082		0.000017
	183.71	0.004028		− 0.000037
Accidental fall in temperature	181.68	0.003968		− 0.000097
	197.03	0.003990		− 0.000075
	215.53	0.004022		− 0.000043
	230.59	0.004022		− 0.000043
	244.87	0.004049		− 0.000016
	255.26	0.004070		0.000005
Maximum	255.26	0.004074		0.000009
	255.26	0.004088		0.000023
	235.44	0.004097		0.000032
	207.52	0.004088		0.00023

Between the fifth and sixth series the apparatus was taken apart, the mercury refiltered, the bulb re-exhausted, and then replaced. The method of measuring the temperature of the copper wire here described and advocated involves considerable more arithmetic labor in computing the results, owing to corrections for barometric pressure, temperature of the mercury column

in the index tube, and expansion in the bulb, but it eliminates all doubt as to the coincidence between the temperature of the wire and the temperature indicated by thermometer, and avoids all differences between the true thermometric scale by air thermometer based upon Boyle's law, and the slightly divergent scale of the ordinary thermometer based upon the expansion of mercury.

Tests of the Copper Wire used. — The resistivity of the wire in the bulb was observed to be 1637 C.G.S. units at 0° C. from its mass and resistance, allowing a specific gravity of 8.90. Several different observations did not agree very closely, however, owing probably to the small diameter of the wire, and its liability to become stretched and variable in diameter.

An analysis of the copper wire used was made by Mr. McCoy of the Purdue Chemical Laboratory and one of the writers. The results are as follows: —

Antimony Arsenic	less than 0.01 per cent;	more than 0.0025 per cent.
Iron	less than 0.025 per cent;	more than 0.0025 per cent.
Zinc	less than 0.03 per cent;	more than 0.0025 per cent.

III.

Note on the Temperature of Lowest Visible Red Heat.

A few measurements were made of the resistance of copper wires enclosed in exhausted glass tubes and gradually raised to just visible red heat, by gradually increasing the current strength through them. The tubes were 30 cm. long, and 2 cm. external, and 1.8 cm. internal diameter. The platinum wires were sealed into the glass at each end, and connected with the copper wire, — one to carry the heating current, and the other to act as "pressure wire," in order to eliminate the resistance of the first, or platinum electrode. The copper wire stretched along the axis of the exhausted tube was 30.4 cm. long, and 0.0015′ (0.0038 cm.) in diameter. Measuring the resistance of these wires at normal temperature with a very feeble current, they were then raised to

redness, and their resistance observed under that condition in a darkened room.

Reckoning back with the linear temperature coefficient of 0.00406 from the normal temperature to zero centigrade, the resistance of the wire was found to be three times that at zero when visible luminosity was just attained, the mean calculated ratio being, in fact, 3.001. If the same linear temperature coefficient be assumed throughout that whole range, the corresponding temperature of lowest visible luminosity becomes 493° C. in this instance.

The method is very sensitive in application, and repeated trials with the same wire and same observer would usually fall within two degrees centigrade by resistance valuation. There was, however, a systematic variation between the observations when the observers were exchanged, amounting to about three degrees of centigrade; and since the criterion of appreciable visibility is merely physiological, it is perhaps impossible to accurately define it. From the sensations experienced in observing, it might be supposed that habit or physical condition would appreciably influence the range of visual appreciation, after the manner of a personal equation.

In conclusion, we desire to express our acknowledgments to Mr. Thomas A. Edison, in whose laboratory the above research was conducted.

ON THE FREEZING-POINTS OF DILUTE SOLUTIONS. II.

BY E. H. LOOMIS.

The Accuracy of the Method.

TWO prominent questions arise in deciding upon the accuracy of the method described in the first part of this paper:[1] —

(1) How much reliance can be put upon the constancy of these fine thermometers?

(2) How much agreement appears in the individual observations of a series out of which the middle is taken?

The former may be best answered from the following table of the freezing-points of water, or determined zero points of the thermometer during the period Oct. 29 to Dec. 4, 1892.

Date.	Observed zero point.	Barometer.	Room Temperature.	Result corrected to 760 mm.
Oct. 29	+0.02900	748.0 mm.	9°.5	+0.03100
31	0.02916	745.0	10°.5	0.03166
Nov. 1	0.02927	743.5	10°.5	0.03202
2	0.02895	748.0	11°.0	0.03095
4	0.03012	755.5	11°.0	0.03087
5	0.03102	756.5	11°.0	0.03160
9	0.03030	757.0	11°.0	0.03080
11	0.03049	755.0	10°.8	0.03112
12	0.03084	752.0	10°.5	0.03217
18	0.03018	750.0	10°.3	0.03185
26	0.03080	759.5	8°.0	0.03088
29	0.03073	759.0	7°.5	0.03089
30	0.03081	756.0	7°.5	0.03148
Dec. 1	0.03000	756.0	7°.0	0.03067
2	0.03096	756.0	7°.0	0.03163
4	0.02893	744.0	7°.0	0.03160

[1] See *Physical Review*, Vol. I., p. 199.

It appears then that the maximum variation in the zero point of the thermometer during the five weeks was 0°.0014. The highest value, +0°.03217, was on Nov. 12; the lowest, +0°.03067, on Dec. 1. A glance at these results forces one of two conclusions — either the thermometer is subject to sudden changes, or the determinations themselves are correspondingly erroneous. Neither of these assumptions is agreeable. The latter is, however, inadmissible, since in such a case the depressions based upon the erroneous zero points would show corresponding errors. This is by no means the fact, and we are forced to admit that the thermometer is subject to slight and dangerously sudden changes which may affect seriously the accuracy of an observation.

The second question is most satisfactorily answered by inspecting a series of observations on any particular solution. For this purpose, as an example of a series where the agreement of the individual observations is least satisfactory, let us choose the $\frac{2}{10}$ normal magnesium sulphate solution. The detailed observations are as follows: —

1 Temperature of protection bath.	2 Overwarming.	3 Overcooling.	4 Reading of thermometer.
− 0°.72	− 0°.330	− 0°.53	− 0°.3867
	0°.335	0°.51	0°.3858
	0°.335	0°.50	0°.3863
	0°.332	0°.49	0°.3858
	0°.330	0°.50	0°.3870
	0°.330	0°.52	0°.3860
	0°.330	0°.52	0°.3859

Barometer = 744.5. Room temperature = 7° C.

As an example of the better series, let us take the one from which the freezing-point of water was obtained on Nov. 12. This selection is made not because the series is especially good, since it is in this particular much surpassed by many others, but because it was in this particular series that the maximum height of the zero point occurred, and the excellence of the series seems to indicate that this sudden change could not arise from an error in

the observations, but more likely was due to actual changes in the thermometer itself. Further, this particular series contains an observation, the first, which was purposely made before allowing the apparatus to cool off to 0° in the "protection bath." I have repeated this experiment many times and always with the result that the observation so obtained is about 0°.004 too high.

1 Temperature of protection bath.	2 Overwarming.	3 Overcooling.	4 Reading.
− 0°.31	+ (?)	− 0°.220	+ 0°.0340
0°.31	0°.160	0°.227	0°.0308
	0°.150	0°.073	0°.0308
	0°.155	0°.065	0°.0308
	0°.165	0°.060[1]	—
0°.29	0°.175	0°.070	0°.0310
0°.31	0°.185	0°.060[1]	—
.	0°.175	0°.070	0°.0308
0°.30	0°.175	0°.065	0°.0310
	0°.180	0°.100	0°.0308
	0°.180	0°.085	0°.0305
0°.30	0°.180	0°.085	0°.0310

Barometer = 752.0. Room temperature = 10°.5.

In the first series it appears the maximum variation is 0°.0012, while in the second it is 0°.0005. In neither case can the middle value be far from the true freezing-point desired.

The Solutions.

These are made first in such concentration that each liter of the solution contains as many grams of the dissolved substance as there are units in its molecular weight. Such a solution is conveniently referred to as a "gram-molecule solution," and its degree of concentration is unity, which we denote by $m = 1$. The temperature to which these standard solutions were referred was 18°, except in the cases of sugar and urea. For the former it was 4°, and for the latter 6°. These standard or gram-molecule

[1] No observation was made, as the overcooling was too little to fall within the prescribed limits.

solutions, in the case of sugar, sodium chloride, and urea, were made by direct weighing of the properly recrystallized and dried substances. In the remaining instances they were obtained from stronger solutions of determined strength by dilution. The strength of these stronger solutions was calculated from their specific gravity by using the tables in Kohlrausch's *Leitfaden der Praktischen Physik* (Leipzig, 1892).

From these data the proper amount of dilution to obtain the required gram-molecule solution is easily calculated. The accuracy of these solutions was ensured by determining their specific gravities, and in the case of the electrolytes by determining also their electrical conductivities. The values are given at the head of each table of results. From these standard solutions the various fractional dilutions were obtained by use of a 200 c.c. flask and suitable pipettes, all of which were most carefully graduated to actual volume. To insure the introduction of the entire contents of the pipettes into the flask, they are rinsed three or more times directly into the flask, and to avoid error in filling, the pipettes are wetted before final filling with equal thoroughness in a special portion of the standard solution. This method is much more expeditious than that of weighing, and is no less satisfactory. The water used in making the solutions is the same as that in which the zero point of the thermometer is determined.

It must be added that organic solutions are made immediately before they are to be used. This was found to be especially necessary in the case of sugar solutions, which showed unmistakable signs of dissolution in less than a week, even at 4° C. It is further necessary to mention that the dilution of the gram-molecule solution in preparing the various fractional concentrations was uniformly done at the temperature of the room, care being observed that the solution and water used in its dilution had the same temperature. Slight errors arising from the different coefficients of expansion of water and the solution are thus possible, but in no way can they affect the character of the results, since the temperature of the room varied only within narrow limits during long periods.

In making the selection of the electrolytes, preference was

given to such as showed great variation in their molecular constitution[1] in the particular region of concentration to which I confine my investigations.

The Results.

In the following table m denotes the strength of the solution in gram-molecules per liter; Δ denotes the depression of the freezing-point, which is *observed* to the fourth place of decimals. The fifth place arises from the reduction of the observations, and has no value except to control the fourth place. The quotient $\frac{\Delta}{m}$ is the molecular depression computed according to Arrhenius, and is furnished directly from the observed data. The quotient $\frac{\Delta}{P/M}$ is the molecular depression as computed according to Raoult, where P denotes the number of grams of the substance dissolved in 1000 g. of water, and M the molecular weight of the substance. To obtain this quotient only the specific gravity of the given solution needs to be known. This was determined for the solution $m = \frac{2}{10}$ in each of the series, and the corresponding value of $\frac{\Delta}{P/M}$ thus directly computed. The values for the more dilute solutions may then be determined exactly enough by lineal interpolation. It is obvious that the two methods of computing the molecular depression lead to essentially different values only in the stronger solutions, and even here the difference is slight except when the molecular volume is large as in the case of sugar.

The results of direct observation are given in ordinary faced numerals in the tables, while the indirectly derived values are given in small-faced type.

[1] F. Kohlrausch, Wiedemann's Annalen, 1885, 26, p. 161.

Sodium chloride, NaCl. $M = 58.51$.
Gram-molecule solution ($m = 1$) at 18° contains 58.51 g. per liter.
Observed Sp. Gr. $_{(18°)}$ 1.0393. Conductivity $_{(18°)}$ $596.4 \times 10.^{-8}$ S.E.
Room temperature, 18°. Time, August, 1892.

Gram molecule in a liter (m).	Depression of freezing-point, Δ.	Molecular depression, $\frac{\Delta}{m}$.	Grams per 1000 grams of water, (P).	Molecular depression reckoned according to Raoult, $\frac{\Delta}{P/M}$.
0.01	0°.03674	3.674	0.585	3.673
0.02	0°.07193	3.597	1.171	3.595
0.03	0°.10680	3.560	1.757	3.557
0.04	0°.14165	3.541	2.343	3.538
0.05	0°.17653	3.531	2.929	3.527
0.06	0°.21172	3.529	3.515	3.524
0.07	0°.24571	3.510	4.103	3.504
0.08	0°.28008	3.501	4.690	3.494
0.09	0°.31448	3.494	5.278	3.486
0.10	0°.34835	3.484	5.865	3.475
0.20	0°.68779	3.439	11.752	3.422
Sp. Gr. $_{(18°)}$ 1.0069				

Cane sugar, $C_{12}H_{22}O_{11}$. $M = 342.07$.
Solution ($m = 1$) at 4° contains 342.07 g. per liter.
Sp. Gr. $_{(17°.5)}$ 1.1286.
Room temperature (4° to 5°.5). Time, February, 1893.

Gram molecule in a liter (m).	Depression of freezing-point, Δ.	Molecular depression. $\frac{\Delta}{m}$.	Grams per 1000 grams of water, (P).	Molecular depression reckoned according to Raoult, $\frac{\Delta}{P/M}$.
0.01	0°.01705	1.705	3.429	1.701
0.02	0°.03545	1.773	6.871	1.765
0.03	0°.05455	1.818	10.334	1.806
0.04	0°.07289	1.822	13.809	1.806
0.05	0°.09210	1.842	17.296	1.822
0.06	0°.11147	1.858	20.798	1.833
0.07	0°.13055	1.865	24.320	1.836
0.10	0°.18971	1.897	34.966	1.856
0.15	0°.28846	1.923	53.008	1.862
0.20	0°.39169	1.959	71.380	1.877
Sp. Gr. $_{(4°)}$ 1.0266				

Magnesium sulphate, $MgSO_4$. $M = 120.46$.
Solution ($m = \frac{1}{2}$) at 18° contains 60.23 g. per liter.
Sp. Gr. $_{(18°)}$ 1.0575. Electrical conductivity $_{(18°)}$ 271.5×10^{-8}.
Room temperature, 7° to 8°. Time, November-December, 1892.

m	Δ	$\frac{\Delta}{m}$	P	$\frac{\Delta}{P/M}$
0.01	0°.02662	2.662	1.205	2.662
0.02	0°.05108	2.554	2.410	2.554
0.03	0°.07420	2.473	3.615	2.473
0.04	0°.09769	2.442	4.820	2.441
0.05	0°.11994	2.399	6.025	2.398
0.06	0°.14171	2.362	7.230	2.361
0.07	0°.16234	2.319	8.436	2.318
0.08	0°.18330	2.291	9.642	2.290
0.09	0°.20348	2.261	10.848	2.260
0.10	0°.22305	2.231	12.055	2.229
0.20	0°.41576	2.079	24.123	2.076
Sp. Gr. $_{(18°)}$ 1.0228				

Ethylalcohol, C_2H_6O. $M = 46.02$.
Solution $(m = 1)_{(18°)}$ contains 46.02 g. per liter.
Sp. Gr. $_{(20)}$ 0.99015.
Room temperature, 6° to 7°. Time, December, 1892.

m	Δ	$\frac{\Delta}{m}$	P	$\frac{\Delta}{P/M}$
0.01	0°.01720	1.720	0.461	1.719
0.02	0°.03510	1.755	0.922	1.753
0.03	0°.05306	1.769	1.769	1.766
0.04	0°.07288	1.822	1.845	1.818
0.05	0°.08936	1.787	2.307	1.782
0.06	0°.10792	1.799	2.770	1.793
0.08	0°.14524	1.816	3.697	1.808
0.10	0°.18253	1.825	4.628	1.815
0.12	0°.21919	1.826	5.561	1.814
0.14	0°.25646	1.832	6.496	1.817
0.16	0°.29269	1.829	7.436	1.811
0.20				
Sp. Gr. $_{(18°)}$ 0.9969				

Sulphuric acid, H_2SO_4. $M = 98.07$.
Solution $(m = 1)_{(18°)}$ contains 98.07 g. per liter.
Sp. Gr. $_{(18°)}$ 1.0615. Conductivity $_{(18°)}$, 3396×10^{-8}.
Room temperature, (0° to − 1°). Time, January, 1893.

m	Δ	$\frac{\Delta}{m}$	P	$\frac{\Delta}{P/M}$
0.01	0°.04493	4.493	0.981	4.492
0.02	0°.08619	4.310	1.963	4.307
0.05	0°.20652	4.130	4.912	4.123
0.10	0°.39679	3.968	9.841	3.954
0.20	0°.76996	3.850	19.762	3.822
Sp. Gr. $_{(18°)}$ 1.0121				

Phosphoric acid, H_3PO_4. $M = 98.01$.
Solution $(m = 1)_{18°}$ contained 98.01 g.
Its Sp. Gr. $_{(15°)}$ 1.0508. Conductivity $_{(18°)}$, 469.7×10^{-8}.
Room temperature, 3°.5. Time, January, 1863.

m	Δ	$\frac{\Delta}{m}$	P	$\frac{\Delta}{P/M}$
0.01	0°.02310	2.310	0.981	2.309
0.02	0°.04344	2.172	1.962	2.170
0.05	0°.10033	2.007	4.912	2.002
0.10	0°.18860	1.886	9.854	1.877
0.20	0°.35828	1.791	19.808	1.773
Sp. Gr. $_{(18°)}$ 1.0091				

Urea, $CO(NH_2)_2$. $M = 60.09$.
Solution $(m = 1)_{6°}$ contained 60.09 g. per liter.
Sp. Gr. $_{(18°)}$ 1.0148.
Room temperature, 6° to 6°.5. Time, February, 1893.

m	Δ	$\frac{\Delta}{m}$	P	$\frac{\Delta}{P/M}$
0.01	0°.01722	1.722	0.601	1.721
0.03	0°.05279	1.760	1.805	1.757
0.05	0°.09067	1.813	3.011	1.809
0.10	0°.18235	1.824	6.037	1.816
0.20	0°.36691	1.835	12.129	1.818
Sp. Gr. $_{(6°)}$ 1.0029				

Remarks on the Solutions.

1. *Sugar.* — It is to be observed that this standard sugar solution is considerably lighter than the usual normal solution based on a liter of solution at 18° C., since in the present case 4° C. was the temperature employed.

2. *Alcohol.* — The solution from which the standard or gram-molecule solution was prepared had Sp. Gr. $_{(20°)}$ 0.9048; and thus, according to the Mendelejeff's tables, was 54.1 per cent alcohol. 85.06 g. should then contain 46.02 g. pure alcohol, and after dilution to a liter volume should give the required gram-molecule solution. Such a solution, however, had Sp. Gr. $_{(20°)}$ 0.99015, and according to the same tables thus appears to contain but 45.65 g. per liter, and appears therefore to be about 1 per cent too light.

It is to be further remarked that the alcohol solutions stronger than about $m=0.10$ *lose alcohol by evaporation*, which occasions a marked and constant rise in the freezing-point during the progress of the observations. These determinations are thus affected by an error. For this reason no observations on the stronger solutions were made.

3. *Phosphoric Acid.* — This solution was made from an acid furnished by Tromsdorff. After an initial dilution its Sp. Gr. $_{(15°)}$ was found to be 1.2490, and thus, according to the tables of F. Kohlrausch, its percentage composition was 39.46 per cent. Accordingly 248.378 g. should contain the 98.01 g. of pure acid required for the standard solution. This amount was diluted to a liter volume, and the Sp. Gr. $_{(15°)}$ was then found to be 1.0508, which, however, corresponds, according to the same tables, to 9.3 per cent, and the solution thus appears to contain only 97.72 g. per liter.

The *conductivity*, on the other hand, is but 469.2×10^{-8}, which corresponds to but 8.7 per cent. I am unable at present to explain these irregularities. It is to be remarked in addition that the solution $m=0.20$, as appears in the table on page 281, has a conductivity 142×10^{-8}, which is almost exactly what the Kohlrausch tables give for this dilution. In this case, as in the case of alcohol, I have applied no correction for this apparent inaccuracy in the gram-molecule solution.

The Correction for Concentration.

It has been mentioned already in the description of the method that the solution is allowed to overcool from 0°.10 to 0°.20 before freezing takes place. In general, this is about 0°.15. The quantity of ice thus formed is small, but is sufficient to occasion a slight increase in the concentration of the solution. Assuming for the present that the latent heat of melting ice (80 calories) is unchanged by the presence of the dissolved substance, and that no heat is given off by the solution save during the actual time of overcooling, theoretical conclusions point to a very simple way of determining the amount of ice which results from any particular degree of overcooling. Thus, an overcooling of 80° C. would result in the complete freezing of the water, while an overcooling of 1° would cause $\frac{1}{80}$ of the water to solidify. In the present instance, when the average overcooling is 0°.15, then $\frac{0.15}{80}$ of the water is frozen, or the solution itself is thus concentrated about 0.2 per cent. The observed depression of the freezing-point is thus about 0.2 per cent too much, and a correction of this extent should be applied. That this, however, is not the true correction — that the change in concentration is considerably *greater*, in fact, than here appears, — is evident; first, because the solution continues to lose heat after the freezing begins (in the present method for two minutes), and consequently the heat removed from the solution is greater than that measured by the degree of overcooling alone; and secondly, the latent heat of melting is undoubtedly less for a solution than for pure water, and consequently a certain degree of overcooling results in a *greater* formation of ice than would be the case for pure water. In the hope of obtaining a more exact correction, I proceeded in various ways, the most satisfactory of which are the following: —

Immediately after making the last observation on the $\frac{2}{10}$ solutions ($m=0.2$), I remove the unfrozen portion of the solution, and compare its specific gravity and conductivity in this slightly concentrated state with those of the original solution. The change in concentration is thus determined. The separation of

the unfrozen portion from the small quantity of fine ice crystals floating in it is easily effected, without any disturbance of the proportion of ice and water, by using a small glass syphon, care being observed to cool this, before insertion, to the exact freezing-point of the solution in a separate portion of the partly frozen solution itself. This was done with the $\frac{2}{10}$ NaCl and the $\frac{2}{10}$ H_3PO_4 solutions, with the following results: —

	Specific Gravity $\left(\frac{18°}{4°}\right)$.		Electrical Conductivity, $k \times 10^{-8}$.	
	Before.	After.	k. Before.	k. After.
$\frac{2}{10}$ NaCl.	1.00692	1.00695	164.40	164.80
$\frac{2}{10}$ H_3PO_4.	1.00967	1.00971	141.96	142.47

The change in conductivity for NaCl was thus 0.24 per cent, while for H_3PO_4 it was 0.35 per cent, which is in close agreement with the corresponding changes in the specific gravities. These changes in specific gravity and conductivity measure the increase in the concentration of the solution, and indicate a correction of about 0.3 per cent to the observed depression. Although this indirect method is quite exact, I was led to make the direct determination in the following very satisfactory manner: the unfrozen portion is drawn off, and treated identically as the original solution. The unfrozen portion is then again drawn off and again treated in the same manner. This is done three times, and the freezing-point of the third portion is then determined. We have thus magnified the concentration threefold; and it is evident that the desired correction is one-third the difference between the final freezing-point and that of the original solution. Still greater accuracy could be obtained by extending the process of successive refreezings to five or six. However, with three refreezings the results confirm the conclusions drawn from the other methods: that the correction is about 0.3 per cent, and thus considerably *larger* than that which is deduced from the mere extent of overcooling; even when, as in the present case, the solution is exposed but a short time

to the action of a very weak freezing-mixture. It seems certain, when the solution is thus exposed many minutes to a very cold freezing-mixture, as is usually the practice in such investigations, that this theoretical correction is wholly unwarranted and inaccurate. The correction, as thus experimentally determined, is still somewhat uncertain; and as its application or omission in no way affects the general character of the results, I prefer to leave them exactly as they were observed. It must, however, be kept in mind that the observed depressions are about 0.3 per cent too great.

The Graphic Representation of the Results.

The best general survey of the results may be obtained when they are graphically represented. For this purpose, instead of the actual depression Δ of a given solution, the quotient $\frac{\Delta}{m}$ is introduced. This is a fictitious depression of this freezing-point, and evidently represents what would be the corresponding depression in a solution of units concentration ($m=1$), if Δ remained proportional to m. This quotient is conveniently known as the molecular depression. The scale of molecular depression, $\frac{\Delta}{m}$, is so chosen that, for $m=0.01$, one scale division represents 0°.001 in actual depression. Thus, an error of 0°.0002 displaces the curve in this region a whole millimeter. This great sensitiveness becomes gradually less in the direction of greater concentration, so that at $m=0.10$, for example, an error of 0°.002 in the observed depression would be required to displace the curve this amount. The course of the curve is thus more certain in proportion as the solutions are more concentrated. The observed points are in general indicated by a cross +, except in urea, where a small circle ⊙ is employed. Since three of the results for urea are identical with those of alcohol, no attempt is made to draw a separate curve.

The curves are drawn by using a flexible ruler, so applied as to best represent the course of the results. The full lines represent the results directly in terms of $\frac{\Delta}{m}$ and m, according to the

method of Arrhenius; while the broken and pointed lines, — · — · —, lying directly below the full lines, represent the same results in terms of $\frac{\Delta}{P/M}$ and m, according to the method of Raoult. The two curves for sugar are widely separated from each other. In the other cases, the two curves are much less widely separated, and in the case of $MgSO_4$ they are so nearly identical that no attempt is here made to draw the second curve.

For the convenience of those especially interested in the question of "disassociation" the theoretical values computed in accordance with the theories of van't Hoff[1] and Arrhenius[2] on the basis of the Kohlrausch[3] determinations of the electrical conductivity of the various solutions are given in dotted lines, and marked "theoretical." As is well known the computation of these theoretical values rests upon the assumption of a certain limiting value for the molecular conductivity in so-called infinitely dilute solutions. This value is in some degree uncertain, and it may be remarked that by choosing a smaller value for this limit in the case of H_2SO_4, say 3600 instead of 3800, the theoretical curve for the molecular depression of the freezing-point becomes much more nearly coincident with actual results of the observations. It needs to be added further that the theoretical values are calculated on the assumption that each H_2SO_4 molecule splits into three parts in the disassociation, and that NaCl and $MgSO_4$ each split into two. No theoretical values are given for H_3PO_4.

Discussion of Results.

A glance at the results as exhibited in Fig. II. reveals an essential difference between the substances which allows them to be grouped in two widely distinct classes. Thus the curves for the four electrolytes, H_2SO_4, NaCl, $MgSO_4$, and H_3PO_4, are convex downward, while the others, the non-electrolytes, sugar,

[1] van't Hoff., Zeit. Phys. Chem., Leipzig, I. p. 496. See also Ostwald's Allg. Chem., 2d. edition, p. 141. The former is translated in the Phil. Mag., 26, p. 95. The second is also published in English.

[2] Zeit. Phys. Chem., I. p. 631. See also Walker, Phil. Mag., 32.

[3] F. Kohlrausch, Wiedemann's Annalen, 26, p. 161, 1885.

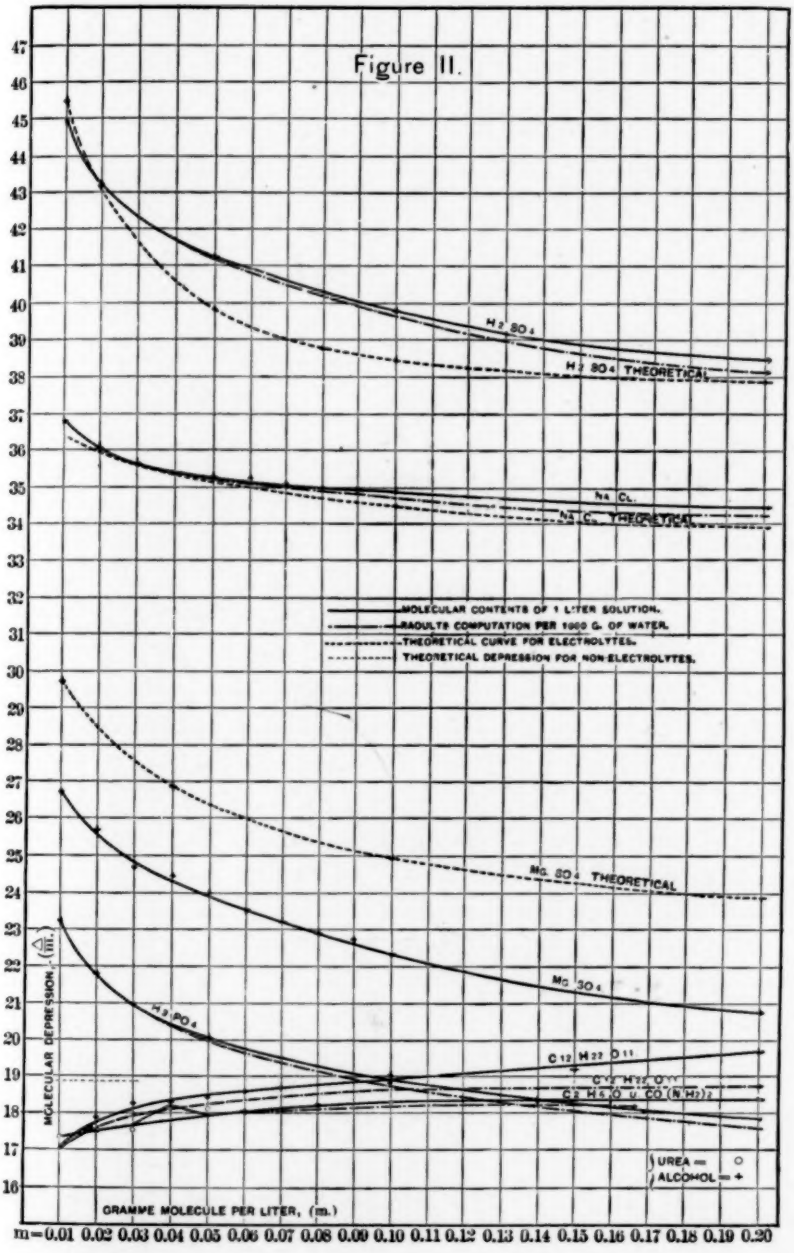
Figure II.
H_2SO_4
H_2SO_4 THEORETICAL
NaCl.
NaCl. THEORETICAL
MOLECULAR CONTENTS OF 1 LITER SOLUTION.
RAOULT'S COMPUTATION PER 1000 G. OF WATER.
THEORETICAL CURVE FOR ELECTROLYTES.
THEORETICAL DEPRESSION FOR NON-ELECTROLYTES.
$MgSO_4$ THEORETICAL
$MgSO_4$
H_3PO_4
$C_{12}H_{22}O_{11}$
$C_6H_{12}O_6$
C_2H_6O u. $CO(NH_2)_2$
UREA = ○
ALCOHOL = +
MOLECULAR DEPRESSION $\left(\frac{\Delta}{m}\right)$
GRAMME MOLECULE PER LITER, (m.)
m = 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.10 0.11 0.12 0.13 0.14 0.15 0.16 0.17 0.18 0.19 0.20

alcohol, and urea, are convex upward. Further, the former, with the exception of NaCl, are thus convex downward throughout their entire length, while in the latter this convexity is only exhibited in the region of extreme dilution and soon gives place to a *straight line.* It is also to be noticed that in extreme dilution the members of the second class have almost identical freezing-points for the same degree of molecular concentration, and that two entirely dissimilar organic bodies, alcohol and urea, have identical freezing-points throughout the region in which they have been studied. Obviously not enough bodies have been studied to lead to any general conclusions, but thus far the two classes are sharply defined.

A comparison of the results with those of other observers in general shows little agreement. However, it is to be observed that the results of Pickering's[1] observations, apart from the irregularities which he found, are very nearly parallel to the present values, and in general lie about 5 per cent higher, which suggests some constant source of error in one or the other series of observations. The striking exception must, however, be noticed in the case of NaCl. Here Pickering's[2] results, when graphically represented as in Plate I., give a curve which crosses the NaCl curve in Plate I. no less than ten times in the region there represented. A scarcely less striking agreement presents itself with H_2SO_4 (*Berlin Berichte*, 192, p. 1106) in the general course of the results, an agreement which becomes a practical identity in the more concentrated solutions. Thus far I have found none of the irregularities which appear in the results of Pickering and which he refers to sudden changes in the properties of the solutions at certain degrees of concentration. I thus no longer make the observations so painfully close together, and the later determinations embrace but five points of observation, which, however, fully fix the general course of the results. I have also found nothing which would indicate that the molecular depression in the case of electrolytes attains a maximum beyond which, in extreme dilution, the depression becomes "abnormally small." The present obser-

[1] Pickering, various contributions, Berlin Chem. Berichte, 1891–92.
[2] Pickering, Berlin Chem. Berichte, 1892, p. 1314.

vations, however, do not reach far enough into this region to make the matter anything but conjecture. However, in the case of NaCl, this maximum appears in Pickering's observations between $m = 0.01$ and $m = 0.02$, where I find no indication of such a turning-point in the values of the molecular depression.

So, too, on the other hand, I have found no "extraordinary increase" in the molecular depression of the organic "indifferent" bodies as the dilution is increased—a fact which would make them resemble the electrolytes, as Traube,[1] Raoult,[2] and Pickering[3] have found. The present results show exactly the opposite tendency on the part of the organic bodies thus far examined.

It is gratifying to call attention to the very remarkable agreement between the present results for NaCl and those recently published by Jones[4]—an agreement reaching to the thousandth degree, even in the more concentrated solutions, which becomes the more remarkable when it is remembered that methods are wholly different. Even had the methods been the same, the use of different thermometers would more than account for all the differences in the two series of observations.

Concluding Remark in Regard to the Accuracy of the Method.

The graphic representation throws much new light upon the accuracy of the method, and indicates that it is not so great as the study of the separate series of observations has led us to believe. To make this evident, attention may be called to the depression as found for the $\frac{4}{100}$ alcohol solution. The value given in the tables and in the curve of results is the middle of seven observations which show a maximum variation of 0°.0005, due mostly to two observations in the series, one of which was as much above the general average as the other was below it. On the assumption that there is no sudden break in the curve at

[1] Raoult, Berlin Chem. Berichte, 1891, pp. 1321 and 1853.

[2] Ann. Chim. et de Phys., 1886, p. 313. Curves for Alcohol and Sugar. Raoult's second determination shows the same tendency, though in a much less degree. See Compts Rendus, 1892, p. 268.

[3] See quotation from Pickering, Berlin Chem. Berichte, 1891, p. 1327.

[4] Zeit. Phys. Chem., XI., p. 110.

this point, we must assume that this observation is more than 0°.0015 too high.

It is interesting to note the history of this particular observation, as it is in some measure a characteristic one. The first observations on alcohol embraced every other hundredth, — thus, $m=0.02$, 0.04, 0.06, etc.

These results, when taken alone, showed a change in the *curvature* of molecular depressions beginning at $m=0.06$. This was so marked that I hesitated to accept the results as final before carefully repeating them with fresh solutions. The three new observations for these points were identical with the original ones, and it became certain that the solution suffered a marked change in properties in this region. To still further confirm the matter, it was determined to find the values at closer intervals; thus, for $m=0.01$, 0.03, and 0.05. There could be no doubt that these would lie so as to still further fix the course of results already so clearly indicated by the observations at $m=0.02$, 0.04, and 0.06.

To my great surprise, the three new observations were not at all in harmony with the observations for $m=0.04$, but indicated another course for the curve as appears in Fig. 2. The conclusion was forced upon me that the method, for an unknown reason, had furnished a result, twice confirmed, fatally inconsistent with all my previous notions of its accuracy. Fortunately, this appears only as an exception, and does not affect one's confidence in the method. It is most probable that such an error is due to some slight impurity on the wall of the thermometer's capillary, which affects the tension of the mercury miniscus at this point, so as to cause it to increase or decrease its curvature slightly at this point, and thus lead to an error in the observation. In all other respects the method commends itself for its great accuracy and simplicity of manipulation.

I wish here to express my deep appreciation of the great help which Professor Kohlrausch rendered me throughout this entire investigation.

PHYSICAL LABORATORY, STRASSBURG,
July, 1893.

MINOR CONTRIBUTIONS.

The Effect of Temperature and of Electric Driving on the Period of Tuning-Forks.

By John S. Shearer.

THE following experiments were undertaken in order to determine: (1) The correction required when an electrically driven fork, whose free period at a certain temperature is known, is used as a standard for the measurement of short intervals of time; (2) The influence of temperature upon the rate of such a fork. The convenience of the driven fork in practical work makes the effect of the various methods of driving of some interest.

The temperature effect for a range from 0° C. to about 30° has been investigated by H. Kayser,[1] and also by A. M. Mayer.[2] Both of these observers used the free fork, however, and made no comparison of the free and forced periods.

In the experiments to be described the method of Lissajous' figures was used to compare the forks, the one vibrating freely under constant conditions, the other driven under the conditions to be studied. The first experiments were made, using a Helmholtz fork-interrupter and a Lissajous vibration microscope. A Morse instrument in circuit with a clock and a signal key was used as a chronograph. The current driving the fork was from a storage battery, and by varying the resistance in the circuit the variations in pitch due to changes of current through the magnets could be determined. The fork used as a standard was bowed, and the other alternately bowed and driven.

It was found that the change in period was in all cases small. In order to keep the apparatus running steadily, a current was required which somewhat increased the amplitude over that observed in the free vibrations, so that the increase of period may have been due to the increased amplitude. The mean of a large number of observations gave 6.43 seconds as the time required for one fork to gain one vibration on the other when both were bowed. When one was driven, the corresponding time was 2.43

[1] Kayser, Annalen der Physik und Chemie, N. F. 8, p. 444.
[2] Philosophical Magazine (5), Vol. 21, p. 286 (1886).

seconds. By means of small pieces of wax, it was found that the change was due to an increase of period of the driven fork. Assuming that the standard made, as marked, 256 vibrations per second, the other when free, made 255.8445 vibrations, and when driven 255.5935. In other words, the free period was .00390863, the forced period .00391246, so that the effect of driving was to increase the period in the ratio of 1 : 1.00098 nearly. Another set the following day, with a slight variation in the tuning, gave for the time of complete change when free 5.92 seconds, when driven 2.78 seconds. The change of rate due to driving was therefore of about the same magnitude as before.

A series of seven resistances giving a range of current suitable for the instrument were then measured, and the forced period was determined for each. This series was repeated several times with consistent results. Tables I. and II. and curve *a* of Fig. 1, give some of the observations and the results derived from them.

TABLE I.

INFLUENCE OF CURRENT UPON RATE OF AN ELECTRICALLY DRIVEN FORK WITH MERCURY CONTACT. [FOUR SETS.]

SET 1.

R	T	N	P	D
11.00	5.18	256.1931	.00391230	00
16.50	5.50	256.1818	.00391248	18
21.66	5.68	256.1761	.00391256	26
29.33	6.04	256.1656	.00391272	42
31.75	6.06	256.1650	.00391273	43
37.75	6.30	256.1587	.00391282	52
41.30	6.94	256.1441	.00391305	75

SET 2.

11.00	5.68	256.1761	.00391256	00
16.50	5.90	256.1695	.00391266	10
21.66	6.06	256.1650	.00391273	17
29.33	6.52	256.1534	.00391291	35
31.75	6.80	256.1471	.00391301	45
37.75	7.40	256.1351	.00391319	63

SET 3.

11.00	4.68	256.2137	.00391199	00
16.50	4.70	256.2128	.00391200	1
21.66	4.84	256.2066	.00391210	11
29.33	5.22	256.1916	.00391233	34
31.75	5.30	256.1887	.00391237	38
37.75	5.44	256.1838	.00391245	46
41.30	5.46	256.1832	.00391246	47

SET 4.

11.00	6.88	256.1453	.00391304	00
16.50	7.20	256.1389	.00391313	9
21.66	7.40	256.1351	.00391319	15
29.33	7.86	256.1272	.00391331	27
31.75	8.38	256.1193	.00391343	39
37.75	9.58	256.1044	.00391366	62
41.30	10.86	256.0921	.00391385	81

Free period for Set 4, .00390387.

Averaging the values of D for each value of R, we get the following results, from which curve a in Fig. 1 is plotted.

TABLE II.

R	= 16.50	21.66	29.33	31.75	37.75	41.30
D (av.) =	9.50	17.25	34.50	41.25	55.75	74.33

In Tables I. and II., R is the resistance in ohms around which the driving magnets were shunted, therefore R is proportional to the current through the magnets; T is the time required for the fork to gain one vibration; N is the number of vibrations per second, and P is the period. D is the difference of period in hundred-millionths of a second.

A small piece of platinum wire touching a piece of metal was next used instead of the mercury contact of the Helmholtz fork, and the position of the magnets was also varied. In each case the change of period was small so long as the amplitude was not greatly increased above that observed for the free vibrations.

For the more extended study of this method of driving, another pair of

forks were used. These were mounted on heavy frames, and the actuating magnets were between the prongs. The microscope was dispensed with, and a ray of light twice reflected was used instead. The circuit was made and broken by means of a platinum spring, attached to the fork, which touched a plate of the same material at each excursion of the prongs outward. This method of driving was found to be more satisfactory than the mercury contact. The fork ran more steadily and could be maintained with a smaller amplitude. The results were the same when the magnets were placed outside the prongs. The observations are given in Table III. with the calculated periods. It will be noticed that for small currents the period is slightly diminished. This was to be expected, since the force of the magnet was added to the recovering power of the fork when the prongs were most widely separated. So long as the amplitude was not considerably increased a slight rise in pitch resulted. With increasing vibration this effect was counterbalanced, and finally the period increased sharply. (See Fig. 1 *b*.)

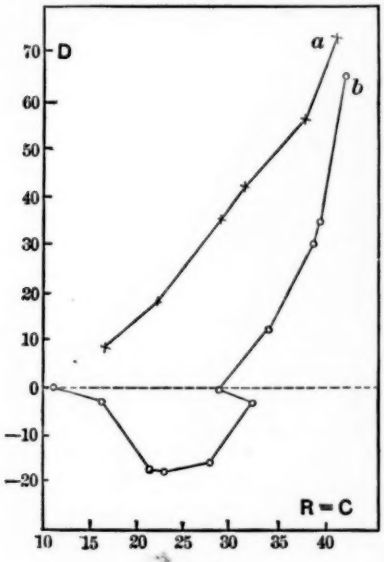

Fig. 1.

TABLE III.

SET 1.

R	T	N	P	D
11.66	3.79	256.2639	.00390223	00
16.90	3.75	256.2667	.00390218	− 5
22.00	3.62	256.2762	.00390204	−19
23.40	3.62	256.2762	.00390204	−19
27.80	3.64	256.2747	.00390206	−17
29.60	3.80	256.2632	.00390223	0
32.80	3.76	256.2660	.00390220	− 3
34.60	3.90	256.2564	.00390234	+11
38.10	4.10	256.2439	.00390253	+30
39.15	4.16	256.2404	.00390258	+35
42.25	4.54	256.2203	.00390289	+66

Free period, Set 1, .00390217.

For the purpose of determining the influence of temperature upon the rate of an electrically driven fork, a coil of German silver wire was placed around the fork and heated by means of a current.[1] To avoid convection currents, the whole was surrounded by asbestos. The temperature was taken by means of two thermometers, one near the base of the fork and the other above. To avoid the effect of increased magnetization of the fork, the heating current was stopped while readings were made, the temperature being observed just before.

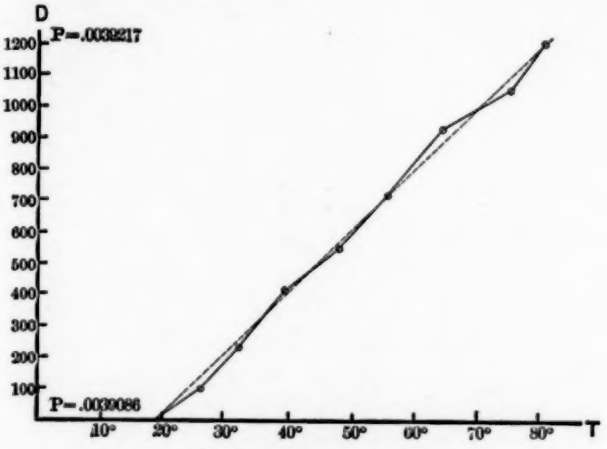

Fig. 2.

It appeared from these experiments just described that for a given current the period was very nearly constant, so that a driven fork, could be used as a standard in the determination of the effect of temperature changes. To make sure, however, that no marked change arose, the standard was frequently compared with a third fork vibrating freely. It is to be observed, however, that the fork becomes magnetized when run by current and this may have a slight effect on the period. By means of a water resistance the current could be varied so as to keep the temperature nearly constant. Readings were taken at intervals of an hour so as to allow the fork to acquire the temperature of the surrounding air as nearly as possible.

The results of a series of observations are given in Fig. 2, the standard being corrected for room temperature under the assumption that its rate of change was approximate to that observed for the other fork. As in the previous cases, D is the difference of period in hundred-millionths of a second.

[1] See this *Review*, Vol. I., p. 147.

The fork heated was made by Koenig, and marked 256 vib. per second. It was about 25 cm. long, 1.85 cm. wide, 1.45 cm. thick. Young's modulus for this fork was determined by method of flexure to be $19.065 \times 10.^{11}$

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
August, 1893.

ON THE CONTINUOUS SPECTRUM OF SODIUM.[1]

BY BENJAMIN W. SNOW.

BUNSEN and Kirchhoff, in their faithful delineation of the spectra of the various metals, detected in the spectra of certain alkalies a faint continuous background upon which the characteristic metallic lines were superposed. This continuous spectrum, which is so faint as to be barely visible in the case of lithium, is more noticeable in the spectra of sodium and potassium, and becomes a prominent feature in the study of the light emitted by burning cæsium and rubidium. During a recent series of investigations, this continuous spectrum was repeatedly observed, and certain data obtained which seem to point to a possible explanation of this phenomenon.

The experiments referred to consisted in the attempt to detect, by means of the bolometer, the presence of infra-red lines in the spectra of the alkaline metals, when the latter were burned in the flame of an ordinary Bunsen burner. It was proved, however, by further investigation that this source of heat is quite insufficient to cause the infra-red lines to appear, and hence the ends sought were not to be attained in this way. Nevertheless, other results of an unexpected nature were obtained, and these may serve to throw some light upon the subject now under consideration.

The apparatus used for detecting and measuring the thermal radiations was a sensitive bolometer, made from fine platinum wire which had been hammered flat and so wound upon a little frame of mica that three threads in series were exposed to the action of the heat. The resistance of each arm of the bolometer so made was 23 ohms.

In order to obtain a galvanometer of greater sensitiveness than any available for use with this instrument, the heavy astatic system of a Siemens galvanometer was removed, and in its place was hung a delicate needle made of short pieces of magnetized steel mounted upon each end of a thin-walled capillary tube.

A fine spectrometer of the usual form and provided with a prism of

[1] Read at the American Association for the Advancement of Science, August, 1893.

dense flint glass served to analyze the radiations to be studied. In place of the cross hairs in the telescope were mounted the sensitive filaments of the bolometer described above, so that these latter served alike for measurements in the visible as well as in the dark heat spectrum. The slit was adjusted in width until its image, as seen in the telescope, was just superposed upon the three threads of the bolometer, and subtended an angle of 20 minutes. This width of slit was retained unchanged throughout the entire series of experiments.

By means of this apparatus an attempt was made to determine the character of the radiation in the infra-red spectrum of an ordinary sodium flame. To this end a Bunsen burner was mounted immediately before the slit of the spectrometer, and in this flame, a few millimeters below the slit, was held a platinum wire containing a bead of sodium carbonate. So small, however, was the quantity of heat thus emitted, that the bolometer, when allowed to wander through the entire spectrum, was quite incapable of detecting, in the very feeble radiation of the Bunsen flame, an increase due to the presence of the sodium.

In order, therefore, to make this flame more intense, an expedient was adopted, whereby the quantity of the incandescent sodium vapor discharged into the flame was greatly increased. The platinum wire holding the bead of sodium carbonate was replaced by a copper spoon three centimeters in diameter, in which were placed little pieces of metallic sodium weighing about one gram apiece. Each lump of sodium, when ignited by the lamp, burned with great violence, and poured into the flame so copious a flood of the incandescent metallic vapor, that the latter, when examined with the spectrometer, produced a *D*-line of unusual brilliancy.

In that portion of the spectrum of shorter wave length than the sodium line, no thermal effects could be detected by the bolometer. So intense, however, was the radiation from this line alone, that a deflection of several centimeters was produced as soon as this line and the sensitive threads of the bolometers were brought into coincidence.

In the remaining portions of the visible spectrum lying toward the red, the quantity of energy was so small that the galvanometer deflections were hardly appreciable. These, however, increased in magnitude as the extreme red end was approached and passed, and continued to increase as the bolometer was moved on from point to point in the direction of the still longer wave lengths, until a region of about $\lambda = 1\ \mu$ was reached, at which point the deflection equalled those produced by the *D*-line. After this, the deflection again decreased, and became zero at wave length $\lambda = 1.8\ \mu$. The infra-red spectrum thus obtained resembled in every respect that produced by an incandescent solid, except that it presented a more or less jagged appearance, depending upon the size of the lumps of

sodium. The presence of so strong a continuous spectrum in the infra-red precluded the possibility of detecting lines in this region, and accordingly this method also was abandoned.

One further attempt in this direction was made, in which the platinum wire with its bead of sodium carbonate was again used, but held now in an oxyhydrogen flame, placed immediately before the slit, instead of the Bunsen burner. Under these conditions, the bolometer showed that the amount of energy contained in the *D*-line was far greater than when metallic sodium had been consumed in the Bunsen burner, but that the energy in the infra-red spectrum had almost entirely disappeared. Beyond the limits of the visible spectrum, the deflections, in fact, nowhere attained a magnitude equal to the one-hundredth part of that produced by the *D*-line.

It was evident, therefore, that the more intense heat of the oxyhydrogen flame had produced a spectrum which differed in two respects from the one arising from burning metallic sodium at a lower temperature. First, the energy of the *D*-line was more than doubled when the more intense source of heat was employed, and second, the continuous spectrum in the infra-red, which had been so prominent when the cooler flame was employed, had almost entirely disappeared.

It has occurred to the writer that a possible explanation of the facts here set forth would be the following: When sodium or a salt of this metal is burned in the flame of a Bunsen burner, the metal unites with the oxygen of the air and produces an oxide which remains suspended in the flame as an *incandescent solid*, at a temperature too low to permit of dissociation. At the higher temperature, however, of the oxyhydrogen flame, the oxide, if, indeed, formed at all, is at once dissociated, and the flame becomes freed from all solid particles which yield a continuous spectrum, and remains filled only with the incandescent metallic vapor, which gives rise to the true line spectrum. If this proposition be granted, it may then be fairly assumed that the faint continuous spectrum, against which the sodium line is so often seen projected, is due, in part at least, to the presence in the flame of particles of incandescent sodium oxide at a temperature too low for dissociation.

PHYSICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN,
October 11, 1893.

Note on Some Surface Tension Experiments.

By Ernest Nichols.

THE writer lately tried to make plain, in a popular lecture, the reasons for some of the phenomena of the surface tension of liquids. There are many ways of showing that a soap-film is elastic and eminently contractile: perhaps the simplest is to show that a soap-bubble is filled with compressed air. This may be done by extinguishing a candle flame with the out-rush of air from a soap-bubble through the bubble-pipe. It is then easy to show some very close analogies between the behavior of soap-films and water surfaces which will make the surface tension of liquids seem a reality to an average audience.

In an interesting experiment with a soap-film described by Van der Mensbrugghe, a loop of moist silk thread is laid on a plane soap-film formed on a ring. The thread enters into the film, and really separates it into two distinct films, — a film within the loop, and a film lying between

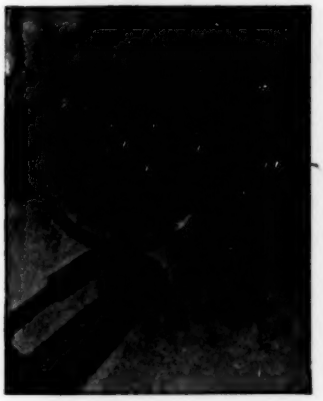

Fig. 1.

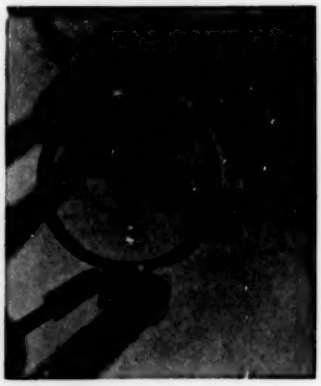

Fig. 2.

the loop and the ring. If the film within the loop be destroyed by touching it with the end of a hot wire, the loop is instantly drawn out into circular form by the pull, equal in all directions, exerted by the outer film upon it. The water surface experiment analagous to Van der Mensbrugghe's is shown by laying a thin rubber band on a clean water surface, and then putting a drop of oil on the water surface inside the loop. The band spreads out considerably, because the oil has diminished the surface tension inside the loop, and the surface tension between the walls of the vessel and the rubber band spreads the loop until the elasticity of the

rubber striving to restore the old form exactly balances the excess of tension of the outer surface over that of the inner. A drop of oil on the liquid surface outside the loop causes a return of the loop to its former

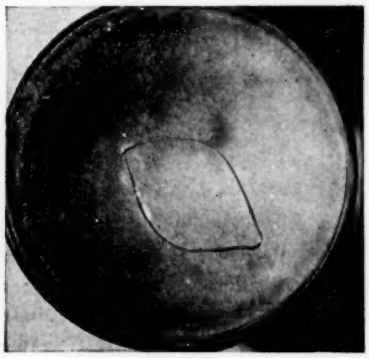

Fig. 3.

Fig. 4.

shape. The thinner and longer the band, the more nearly circular will be the expanded loop.

Figs. 1 and 2 are from photographs of the two stages in Van der Mensbrugghe's experiment; and Fig. 3 is from a photograph of a rubber band on a water surface, taken after the loop has been expanded by a drop of oil placed inside it. Fig. 4 is the form to which the band returned when oil was placed on the outlying surface as well.

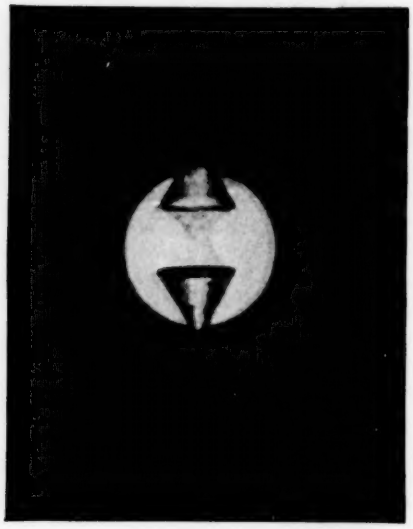

Fig. 5.

Two soap-bubbles blown on glass funnels, and then crowded together, can be made to unite, giving a single film which depends for its form, at any time, on the distance separating the funnels. When the funnels are pulled farther and farther apart, the film becomes spindle-shaped, with a neck more and more constricted, until finally the two bubbles spring apart. This experiment can be repeated in miniature with two drops of water on the ends of two glass tubes. The similarity of behavior of the drops of

water and the soap-bubbles, and the resemblance in the curves shown in the process of separation in the two cases are striking.

Fig. 5 is from a photograph of a soap-film, and Fig. 6 shows a stage in the separation of two drops of water. A similar analogy appears between the way in which a soap-bubble leaves the bubble-pipe and the separation of a drop of liquid from the tip of a burette. A water surface seen "edge on," which is supporting a globule of carbon bisulphide colored with iodine is of interest in this connection. This is an experiment of another sort, but the curved outline of the water surface sagging beneath the weight of the heavier carbon bisulphide is a manifestation of surface tension, and the experiment is a significant one. The experiments described are all easily put into the lantern for projection, and are best shown in that way.

Fig. 6.

COLGATE UNIVERSITY, HAMILTON, N.Y.,
July, 1893.

NOTE.

John Tyndall. — In the passing away of John Tyndall, whose death occurred at Haslemere, England, on the 4th of December, 1893, Physics loses one of her chief votaries. No man of science of his generation has been more widely known than he; very few have exerted a wider influence.

John Tyndall was born on the 21st of August, 1820, at Leighlin Bridge, near Carlow, in Ireland. He was the son of an Irish constable, and a direct descendant of the martyr, William Tyndale, who was burnt at the stake in the sixteenth century. Although in humble circumstances, Tyndall's father was able to keep his son in the local schools until the latter was nineteen years old, at which time he became a member of the Ordnance Survey. In 1843 young Tyndall became a railway engineer in England, which calling he followed for three years, when he resigned his post to become a teacher in Queenwood College. Doubtless his first experience as a teacher made clear to his own mind his deficiencies of preparation. He was already a reader of Carlyle, and it was due to the influence of the latter that he turned his face toward Germany for further study.

Marburg was at that time a seat of great scientific activity. Bunsen was professor of chemistry there, Stegmann of mathematics, and Knoblauch of physics. Under these men he studied and with them became a co-worker. Subsequently, in Berlin, 1851, he worked in the laboratory of Magnus, and made the acquaintance of Riess, Clausius, Wiedemann, and Poggendorff.

It was at the suggestion of Knoblauch, in 1849, that he began the study of diamagnetism, a subject to which he was destined to devote several years of his life. His first paper, published in *Poggendorff's Annalen*, Vol. 79, 1850, and in the *Philosophical Magazine* of the same year, was the result of a joint investigation made in collaboration with that physicist on *the deportment of crystalline bodies between the poles of a magnet.* The publication of this paper had a direct bearing upon Tyndall's subsequent career, for it served as a favorable introduction to Faraday, upon whom he called when he returned to England. Faraday, himself the discoverer of diamagnetism, was impressed with the valuable character of Tyndall's work, and he secured him an invitation to lecture at the Royal Institution.

This lecture was delivered on February 11, 1853, and in July of that year Tyndall was elected Professor of Natural Philosophy in the Royal Institution.

The Royal Institution, from the time of its foundation by Count Rumford to the present day, has been the scene of the most brilliant experimental demonstrations known in the history of physics. It was there that Davy, in 1807, exhibited the first electric arc light; that Faraday announced his many discoveries, demonstrating them to delighted classes. Under Tyndall, who was the follower of Davy and Faraday in this renowned chair, the Royal Institution lost none of its fame.

Tyndall's power as a popular writer of science was so extraordinary that his attainments in this field have largely overshadowed his other work. It is of his lectures on sound and on light; of his books on *Heat as a Mode of Motion*, on the *Forms of Water*, and on the *Glaciers of the Alps;* of his essays as embodied in the *Fragments of Science*, and in the *New Fragments*, that we think when we hear Tyndall's name spoken, rather than of his work as an investigator. And yet, for the quarter of a century during which these books appeared, he was indefatigable in original work. The Royal Society Catalogue gives seventy-two titles of memoirs under his name, previous to 1864, and the supplement covering the ten years following, including 1873, adds forty important papers to the list. The range of subjects is a wide one; but the fields of his activity in research were, roughly speaking, the following: magnetism and diamagnetism, to which he devoted his attention chiefly during the decade 1850–'60; the domain of radiant heat, which occupied his continual attention for ten years following; the study of the atmosphere with particular reference to the formation of clouds and the color of the sky, a theme which led up to the study of properties of smoke and dust in the atmosphere, and so finally to his last great work upon atmospheric germs.

The conclusions which he reached concerning the floating matter in the air were embodied in his famous lecture on *Dust and Disease*, which was delivered at the Royal Institution in 1870. The battle which ensued was long and severe. It resulted in the establishment of the germ theory of disease, an achievement in which Tyndall and Pasteur will always share the honors. During all these years of his scientific activity, Tyndall spent his summers in the Alps. He was one of the most intrepid and successful of mountain climbers, and he was also an enthusiastic student of the phenomena presented by the Swiss glaciers. It is to these vacation studies that we owe some of his most fascinating books, and it is upon them that no small portion of his fame rests.

In addition to his original work in physics and to his studies of the glacier ice, Tyndall was for many years one of England's chief writers in

the field of speculative philosophy and of general science. His work in this field deserves to rank with that of his life-long friend, Professor Huxley. First among these essays, perhaps, stands his address as President of the British Association, in 1874. It was in this Belfast address that Tyndall enunciated his view with reference to the origin of life. "Believing as I do in the continuity of nature, I cannot stop abruptly where our microscopes cease to be of use. Here the vision of the mind authoritatively supplements the vision of the eye. By an intellectual necessity, I cross the boundary of experimental evidence and discern in that *matter*, which we in our ignorance of its latent powers, and notwithstanding our professed reverence for its Creator, have hitherto covered with opprobrium, the promise and potency of all terrestrial life."

This daring declaration shook philosophic England to its center. Protests against its materialism arose in many quarters. The discussion which ensued was one of the most notable of that time. Its very echoes have died away now, and if we may judge them by their later utterances the school whose views were embodied in the Belfast address has materially changed its attitude. Tyndall, himself in fuller explanation of his point of view, assumed a much more conservative position.

While Professor Tyndall stands in the first rank of the speculative writers of his time, he stands in another important field entirely alone. As a popular writer upon the phenomena of physics he has had no equal. Remarkable as an investigator and remarkable as a writer of English, it is after all to his wonderful power in describing the beauties of natural philosophy that he owes his chief fame. The aim which he professes in his books is, at first sight, a simple one. In the preface to his *Lectures on Sound*, he says: "In the following pages I have tried to render the science of acoustics interesting to all intelligent persons, including those who do not possess any special scientific culture." The preface to *Heat as a Mode of Motion* begins in almost the same words: "In the following lectures I have endeavored to bring the rudiments of a new philosophy within the reach of persons of ordinary intelligence and culture. . . . My aim has been to rise to the level of these questions for a basis so elementary that a person possessing any imaginative faculty and power of concentration might accompany me." To the fulfilment of this purpose, gifts, more unusual than those of the scientific investigator or those of the writer of speculative essays, are necessary. These gifts Tyndall possessed in the highest degrees, and he has utilized them for the delight and inspiration of an entire generation.

E. L. N.

NEW BOOKS.

Light and Other High-Frequency Phenomena. By NIKOLA TESLA.

Introduction. — Mr. Tesla introduces his lecture about as follows: — In our study of the physical universe we find that our sense of sight is superior to all other senses, because it enables us to penetrate much deeper into the fathomless depths of Nature's mysterious activities. The activity by means of which Nature reveals herself to us through our organ of sight, the activity which we call light, deserves our closest attention. What is light? It is an electromagnetic activity, according to most advanced views; hence the importance of investigating those forms of electromagnetic activities which approach the phenomena of light as near as experimental possibilities of the present day will permit.

The introduction might lead one to expect that Mr. Tesla intends to describe a novel class of high-frequency electrical oscillations for the purpose of illustrating and giving new evidence in favor of the electromagnetic theory of light. In that case one would perhaps feel somewhat disappointed to find that Mr. Tesla's experiments are simply Hertz's experiments in a modified form, a form by which it can be shown that in the first place the Hertzian oscillations enable us to transmit a considerable amount of energy along a single wire, and in the second place that novel vacuum tube effects can be produced by rapid alternations of the electromagnetic field.

But this feeling of disappointment, if it should occur at all, would be soon dispelled and quickly give way to a feeling of admiration for the patient work of an enthusiastic inventor who has brought all the ingenuity of his remarkable engineering skill to bear upon the problem before him, and that problem is contained in the question: — What immediate benefits can modern electrotechnics derive from Hertzian oscillations? This problem Mr. Tesla handles with extraordinary ability.

Method of Conversion. — To produce the oscillations Mr. Tesla connects a direct or alternating current dynamo to an oscillatory transformer. The primary of this transformer, consisting of a small number of turns of stranded wire, corresponds to the Hertzian exciter, and the secondary, consisting of an appropriate number of turns of wire surrounding the primary, corresponds to the Hertzian resonator. Hertz worked with oscillations of about 10^8 periods per second. Mr. Tesla is satisfied with a

frequency of 10^6 or even smaller, hence his primary and secondary coils have a much larger self-induction than that of the Hertzian exciters and oscillators. By a suitable arrangement of the ratio of the turns in the primary and secondary, the oscillatory transformer can be an up or a down transformer. The primary spark space is similarly located as in the Hertzian experiments. Capacity is generally added to both the primary and the secondary coils.

Precautions which must be observed in order to render the Primary Impulses very Powerful. — No arc formation should be allowed in the primary spark space. Four different devices for this purpose are described, the purpose of each being to blow out the arc as soon as it begins to form.

1. Spark space is placed between the poles of a sufficiently powerful magnet.

2. Current of hot air sweeps continually through the spark space (especially when dielectrically weak air is required between the discharge knobs).

3. Spark space is placed in a partially exhausted glass tube, the tube being placed between the poles of a strong magnet to prevent arc formation.

4. Two objections against a spark space through a gaseous medium are pointed out: (*a*) the discharges are not sufficiently disruptive; (*b*) there is too much dissipation. To improve both, a liquid dielectric was tried. A hollow pulley was partially filled with oil (the quality of oil not mentioned); the pulley being rotated rapidly, the oil was thrown out centrifugally and compressed against the rim; discharge through oil improved the disruptive character of the primary sparks and diminished losses. These discharges were effective for producing great spark length, but not for luminous effects, since for these, according to Mr. Tesla, a harmonically varying electromagnetic force is preferable.

The best form of generator is then discussed; it is pointed out that the most convenient method is to use a low-tension dyna-motor, to transform direct currents into low frequency alternating currents of low voltage. The low-voltage alternating current thus obtained is then transformed into high tension alternating by a stationary transformer, and this high-tension current is then employed to feed the oscillatory transformer.

Phenomena produced by Electrostatic Force. — In the introduction to these phenomena, Mr. Tesla makes the following statement concerning electrostatic force: "It is the force which governs the motion of the atoms, which causes them to collide and develop the life-sustaining energy of heat and light, and which causes them to aggregate in an infinite variety of ways according to Nature's fanciful designs, and to form all these wondrous structures we perceive around us. . . ."

Evidently Mr. Tesla makes even a broader claim for the electrostatic

force than Professor J. J. Thomson does for Faraday's tubes of electrostatic induction. (Compare also H. von Helmholtz's lecture on Faraday.[1])

Experiment 1. — One pole of the oscillatory transformer is touched with one hand, and the other hand approaches the other pole. A brush discharge passes from the free hand to the free pole. The frequency of the current is said to be a million, and the electromotive force $= 2 \times 10^5$ volts. Mr. Tesla calculates that, with four times the frequency, and a potential of 3×10^6 volts, his whole body would be surrounded by a flame, but the current would do him no harm, because the body offers a large cross-section to the high-frequency current, and the current *in its passage through the body distributes itself uniformly*, so that the current density is small at any point. This interpretation takes it for granted that Hertzian oscillations pass through the human body just the same as an ordinary direct current would pass through a good conductor.

Experiment 2. — Illustrates difference between discharges at high and low frequency. Two circular brass plates, each connected to a pole of an oscillatory transformer, are placed at a distance of 12 inches. At high frequency the luminosity of the discharge between the plates is steady and perfectly uniform; at low frequency, the discharge is in the form of numerous, quivering, and noisy spark filaments. Mr. Tesla admits the impossibility of disruption at high-frequency; he observes the powerful chemical action of the high-frequency discharge; he seems, however, to fail to recognize in the difference of the two discharges a confirmation of the generally accepted dissociation theory of electrical conduction through gases.

Experiment 3. — An incandescent lamp bulb with a single straight carbon filament is attached to one pole of the oscillatory transformer. An apparently unipolar discharge takes place. (The luminosity in the immediate neighborhood of the external surface of the lamp is evidently due to the varying condenser charges of that surface. If that surface has any sharp points, the current density there will be large, and the point will be heated.[2]) A bulb drawn out into a point is (therefore) heated and is ultimately broken at that point. Mr. Tesla ascribes this heating to molecular bombardment which, according to his opinion, will take place in *heterogeneous media like gases*, because *the molecules* or atoms in such bodies are free to move under the impulse of electrical forces. Mr. Tesla does not seem to be aware of the fact that nobody has succeeded yet in electrifying the molecules of a perfect gas. Several experiments are then described in support of the bombardment theory, but they do not seem to be convincing.

[1] Vorträge und Reden, Vol. 2, p. 302, 1884.

[2] The reviewer is responsible for the opinion enclosed in parentheses in this paragraph.

On Currents or Dynamic Electricity Phenomena. — In these experiments it is shown that electrical energy can be transmitted along a single open-circuited wire. The *modus operandi* is the following: — One end of a wire is attached to one of the poles of the secondary of an oscillatory transformer; the other end is attached to a large plate. An adjustable coil is also inserted in this circuit. The plate gives this open circuit its principal capacity, the adjustable coil, which the reviewer calls the inertia coil, enables the experimenter to regulate its self-induction or inertia. When the frequency is very high, the capacity of the plate can be dispensed with, the capacity of the remaining part of the circuit being sufficient to bring the circuit in resonance with the impressed electromotive force.

Two methods are then employed to demonstrate the flow in the open circuit and its dependence on the constants of the circuit; namely, capacity, self-induction, and frequency.

Method I. — The circuit of several turns of wire surrounding the auxiliary inertia coil is closed by a 50-volt, 16-C.P. lamp, and the flow studied by the intensity of the glow of this lamp.

Method II. — The flow in the open circuit is transformed in various ways, and various simple devices are then employed to cause a disc to rotate under the electromagnetic or electrodynamic action of the oscillatory currents thus employed. The first method points out the possibility of a distribution of oscillatory currents for electric lighting; the second method demonstrates in a certain way the feasibility of employing such currents for operating electromotors. The difficulties which would necessarily attend such an employment of oscillatory currents might have been discussed a little more fully, in order to prevent a misconception on the part of those who are not familiar with the subject. To show the effects of impedance (a wave distribution of potential energy along a short, stout wire), Mr. Tesla employs Lecher's well-known and generally adopted method of producing very rapid Hertzian oscillations. He devotes, then, twelve pages to a discussion of electrical resonance, and particularly of the bearing of electrical resonance upon the problem of transmitting signals all over the earth by causing the electrical charge of the earth to oscillate.

This discussion is evidently introduced to relieve somewhat the serious character of the rest of the lecture, and seems to bear the same relation to the rest of the lecture as the amusing gravediggers' dialogue in "Hamlet" bears to the rest of the play. In the reviewer's opinion, Mr. Tesla does not wish to be taken *au serieux* in this part of his lecture.

Vacuum Tube Effects produced by Hertzian Oscillations.

1. *Incandescence of a Solid.* — It was observed a long time ago that the electrodes of a Geissler tube, especially the cathode, become very hot, although the current through the tube may be exceedingly small.

Mr. Crookes, it seems, was the first to suggest that this heating was due to molecular bombardment. Mr. Tesla shows that by means of this property of the vacuum-tube discharge carbon filaments and carbon buttons, when enclosed in the vacuum of an incandescent lamp, can be rendered incandescent by an exceedingly small current, provided that the potential of these carbons is very high and the frequency considerable; the higher the frequency, the slower will be the process of disintegration of the carbons. He also ascribes this heating to molecular bombardment, but his arguments in favor of this view are open to the same objections which were brought, long ago, against the molecular bombardment theory of Crookes. Some of the heating in such tubes is very probably due to molecular, or rather atomic, bombardment, but according to the splendid investigations of E. Wiedemann, Schuster, Elster and Geitel, J. J. Thomson, Giese, and others, the chemical process going on in such tubes owing to the action of the electrical forces will account easily for a very large part of the heat. It should also be remembered that the spectrum of an incandescent gas is very rich in ultra-violet light, which part of the luminous energy of the gas never leaves the bulb, being absorbed by the same and transformed into heat. To ascribe all the various heat phenomena in a vacuum tube simply to molecular bombardment means to turn a sharp corner, in order to get out of the way of difficulties instead of forcing the difficulties themselves to get out of the way. The same criticism applies to Mr. Tesla's view of the cause which produces phosphorescence and fluorescence in vacuum tubes. It is, of course, a well-known fact that mechanical shocks can produce phosphorescence and fluorescence; but it is equally well known that no agent is as powerful as ultra-violet light and purely chemical processes to produce these phenomena. Why, then, refer these phenomena in vacuum tubes to molecular bombardment and to nothing else?

It must be observed, however, that the value of Mr. Tesla's work is, of course, independent of the view which he may have formed of the causes of all these various phenomena which he investigated by means of extremely powerful electrical oscillations. The real value of Mr. Tesla's work is due to the fact that he was the first to succeed in constructing a magnificent array of physical apparatus, by means of which these exceedingly powerful Hertzian oscillations can be produced, and to point out a way of attacking old but still puzzling phenomena by weapons with which the refinements of modern electrotechnics can furnish us. It is a work which, for some time to come, will be consulted by the electrical engineer who wishes to become acquainted with the tendencies of recent advances in electricity, and it will be consulted by the physicist who wishes to make himself familiar with the practical bearing of these advances. In the per-

formance of this work Mr. Tesla has, therefore, rendered invaluable service to all those who are interested in the science of electricity.

M. I. PUPIN.

COLUMBIA COLLEGE, New York, Oct. 15, 1893.

Two Treatises on the Theory of Elasticity.[1]

Mr. Love's volume treats the mathematical theory of the elasticity of bodies of finite dimensions. A second volume, according to the plan announced by the author, is to treat the theory of the elasticity of bodies, some of whose dimensions are so small as to be considered infinitesimal. The present volume is well arranged. The order of treatment is as follows: Chap. I., 21 pp., Analysis of Strains; Chap. II., 12 pp., Analysis of Stress; Chap. III., 73 pp., Stress-Strain Relations; Chap. IV., 9 pp., Strength of Materials; Chap. V., 36 pp., General Theorems; Chap. VI., 53 pp., Saint-Venant's Problem; Chap. VII., 33 pp., Curvilinear Co-ordinates; Chap. VIII., 16 pp., General Solutions; Chap. IX., 25 pp., The Problem of an Infinite Solid bounded by a Plane, Boussinesq and Cerruti; Chap. X., 36 pp., The Equilibrium of the Sphere, Lamé; Chap. XI., 22 pp., The Vibrations of the Sphere; Chap. XII., 14 pp., Application of Conjugate Functions.

Chap. III. deserves special mention. It contains an exhaustive treatment of the general theory of elastic constants and a good sketch of crystallography. Chap. IV. is very brief, but, with references given to universally accessible writings, it is essentially complete. Chap. V. gives a brief and satisfactory sketch of the development of the theory of stress-strain relations from Cauchy's point-atom hypothesis, and a number of general theorems concerning possibilities and uniqueness of solutions, energy function, wave motion, and free vibrations of solids. Chap. VII. gives a more than ordinarily clear exposition of curvilinear co-ordinates.

The mathematical developments are very concise and elegant. The notation is simple and straightforward, and is based upon precedent. In arranging the plan of treatment the author has evidently been guided by a consideration of the present state of English literature on the subject, and has avoided extensive treatment of many topics, such, for example, as the natural history of elasticity, and the elaborate theory of types of stress and strain, both of which topics are so admirably treated in the generally accessible writings of Sir W. Thomson (Lord Kelvin). An historical introduction of thirty-four pages is well placed. The author has wisely

[1] *A Treatise on the Mathematical Theory of Elasticity.* Vol. I. By A. E. H. LOVE, M.A. 8vo, pp. 354. Cambridge, University Press, 1892.

Leçons sur la Théorie de l'Élasticité. Par H. POINCARÉ, Membre de l'Institut. 8vo, pp. 208. Paris, Georges Carré, 1892.

followed the plan of dividing the text into distinct paragraphs, each with prominent heading, and each strictly limited to a point in question. This fact, together with the exhaustive table of contents and a good index, will go far towards rendering the book readily useful for reference. No problems are given. Mr. Love has introduced but few if any novelties of nomenclature. We cannot refrain from expressing at this point our preference for such expressions as bulk-modulus, slide-modulus, and stretch-modulus, to such expressions as modulus of rigidity, Young's modulus, and the like. Some writers even use the expressions, "coefficient of volume elasticity," "coefficient of simple rigidity." Mr. Love uses the name, bulk-modulus, but not the others. They have been occasionally used, however, and with evident clearness and brevity.

If Vol. II. come up to the high standard of Vol. I., Mr. Love's treatise will be a valuable addition to the literature on elasticity. It shows no tendency to undue simplification. Its scope is by no means narrow. Its style, being concise, is such as to stimulate the study of other works, and particularly of original memoirs. The realization of such tendency is rendered possible by reason of numerous choice references. On the whole, it would seem that the work must be admitted to first rank in the series of mathematical treatises for which Cambridge is justly celebrated.

M. Poincaré's book is written in the same attractive style as his "Electricité et Optique" and "Thermodynamique." To English readers particularly it must, however, prove less satisfactory. In his preface to "Thermodynamique" the author says, "*Abandonnant les théories ambitieuses d'il y a quarante ans, encombrées d'hypothèses moléculaires, nous cherchons aujourd'hui à élever sur la Thermodynamique seule l'édifice tout entier de la Physique mathematique.*" Now precisely the most serious objection to the "Leçons sur la Théorie de l'Élasticité" is that the treatment of stress-strain relations is made to rest upon Cauchy's point-atom hypothesis — an hypothesis so particular in its assumptions as not to be susceptible of adaptation to broad lines of experimental fact. English readers, being so familiar with Lord Kelvin's writings, cannot now have patience with such a method. Nothing can be more nearly free from misleading particularization than the assumption that the stress at a point in a body is a function of the strain at that point. That part, if any, of the stress which does not vanish with the strain being ignored, then if it be assumed that linear terms and terms of higher order only appear in the expansion of this function, Hooke's law in its most general aspect follows at once for infinitesimal strains, which only are considered at present in the mathematical theory of elasticity. Further, there would be a wide discrepancy between this theory and experience if these assumptions were not in the main legitimate. These assumptions involve Lord Kelvin's

definition of perfect elasticity (see *Ency. Brit.* "Elasticity"), which we know to be satisfied with high approximation for many substances through comparatively wide limits of strain. For infinitesimal strains, too, we must remember that the rates of change of the strains are also infinitesimal, so that it is probable that Hooke's law is legitimate for infinitesimal strains for substances which exhibit marked viscosity under varying finite strain. Hooke's law may then be considered a formal axiom justified by experience for infinitesimal strains. Lord Kelvin's application of the laws of thermodynamics in the proof of the existence of the energy function establishes the mathematical theory of elasticity on a thoroughly satisfactory basis.

The notation employed by French writers is perhaps something which no English reader has a right to criticise. Yet English translations of recent French treatises on mathematical physics are often targets in this respect. Witness, for example, the translation of Mascart and Joubert's "Electricity and Magnetism." The "Leçons sur la Théorie d'Élasticité" must be considered decidedly the weakest of M. Poincaré's works in this respect.

Theoretical science has a strong historical perspective. Its present aspects must always be most vital, and remote things must continue to grow less explicitly important. Yet undue haste in disregarding the classic is no less fatal here than elsewhere. A student must not be led to think that any systematic treatise, however well written, can relieve him of the necessity of studying the classics of his subject. M. Poincaré's "Leçons" is not satisfactory in that it is not calculated to incite a student to a vigorous pursuit of the subject. It is poor in its method, narrow in its scope, and fragmentary in its choice of material. It gives no references to original sources. We have nowadays an increasingly large number of books which grow out of the limited experience of a teacher in handling a short course of lectures on a subject. To presume to rank such works with extensive treatises is, of course, preposterous; to judge them by the same standard is manifestly unfair. Some books are written that everybody may know something; some, on the other hand, are written that somebody may know everything. The object of writing is often immediately and apparently the former, but always and really the latter.

W. S. FRANKLIN.

NOTE. — Just as the above is going to press, Volume II. of Love's Treatise[1] appears. A hasty examination produces a very favorable impression, and it seems that the promise of the first volume is fulfilled. An historical

[1] *A Treatise on the Mathematical Theory of Elasticity.* Vol. II. By A. E. H. LOVE, M.A. 8vo, pp. 327. Cambridge, University Press, 1893.

introduction to the theory of the elasticity of thin rods and plates, 23 pp., with many choice references, amounts almost to a bibliography of that subject. The arrangement is as follows: Chap. XIII., 25 pp., The Bending of Rods in One Plane; Chap. XIV., 24 pp., The Bending and Twisting of Rods in Three Dimensions; Chap. XV., 21 pp., General Theory of Thin Rods; Chap. XVI., 21 pp., Theory of the Small Vibrations of Thin Rods; Chap. XVII., 21 pp., Resilience and Impact; Chap. XVIII., 30 pp., General Theory of Wires Naturally Curved; Chap. XIX., 25 pp., Elementary Theory of Thin Plates; Chaps. XX. and XXI., 44 pp., General Theory of Thin Plates and of Thin Elastic Shells; Chap. XXII., 44 pp., Applications of the Theory of Thin Shells; Chap. XXIII., Stability of Elastic System.

The treatment of rods and plates can hardly be expected to be as satisfactory as the treatment of the general theory of elasticity, and it is surely not so well known to students. Chaps. XIII. to XVIII. seem, however, to be thoroughly satisfactory, and Chaps. XIX. to XXII. are perhaps as satisfactory as they can be, considering the difficulties of the theory of plates and shells.

Mr. Love has clearly demonstrated that there was need of a good treatise on the theory of elasticity by writing one.

W. S. F.

The Science of Mechanics. By Dr. E. MACH. Translated by T. J. MCCORMACK. 8vo, pp. x+538. Chicago, The Open Court Publishing Co., 1893.

In looking through a library of text-books one must be struck by the great number of books on mechanics as compared with the number in other departments of physics. This arises from the fact that mechanics is the oldest branch of physics. But there is another and more important reason, and that is the difficulty of stating the fundamental principles, there being a selection of methods of statement. A study of the volume before us will tend to lessen the multiplication of books, as it will show the dissatisfied reader that though possibly he might make another selection, it would not necessarily be an improvement.

Mach's "Mechanics" is unique. It is not a text-book, but forms a useful supplement to the ordinary text-book. The latter is usually a skeleton outline, full of mathematical symbols and other abstractions. Mach's book has "muscles and clothing," and being written from the historical standpoint, introduces the leading contributors in succession, tells what they did and how they did it, and often what manner of men they were. Thus it is that the pages glow as it were with a certain humanism, quite delightful in a scientific book.

Recognizing that mechanical ideas have been evolved from the investigation of simple and special cases of mechanical processes, the method of the book is the historical. The development of the science is shown to cluster around a few great names. Beginning with the investigations of the ancient Greeks concerning equilibrium, the development of the principles of statics is sketched in the first quarter of the volume. The next half of the volume is devoted to an account of the development of the principles of dynamics, and the balance to an account of the more modern extensions of dynamical principles. Here we find D'Alembert's principle, the principle of kinetic energy, of least action, etc., all treated with a minimum of mathematics, but with a maximum of illustration. Throughout the book the method of presentation is to give the discoverer's account of the proposition presented as nearly as possible in his own way. Next follow criticisms of the proposition or of its proof, and perhaps a supplemental proof is given. Then come general observations on the underlying principle, and it may be on the author himself or his methods. Thus, contrasting Stevinus's conception of the inclined plane with that of Galileo, Mach remarks, "It is in this fact that Galileo discloses such scientific greatness: that he had the *intellectual audacity* to see, in a subject long before investigated, *more* than his predecessors had seen, and to trust to his own perceptions." And again, "Newton's reiterated and emphatic protestations that he is not concerned with hypotheses as to the causes of phenomena, but has simply to do with the investigation and transformed statement of *actual facts*, stamps him as a philosopher of the *highest* rank."

There is a very full account of the units used in dynamics though some of the notation is rather antiquated. Surely, for example, it is time to drop *vis viva*, *quantity of motion*, *conservation of force*, and the like. The definitions of mass and weight given are those accepted by physicists, but not by engineers — quite as important a body.

To many the most interesting part of the book, as it is certainly the part most provocative of thought, will be the section in which Newton's laws of motion are discussed, and in which it is urged that the time has come for a restatement of these laws. That there is a necessity for a restatement few will deny, but it is to be doubted if the substitute proposed by Mach will be accepted. Still the discussion is most timely, the subject occupying as it does just now so much of the attention of English and American physicists.

With German thoroughness our author explores not only the highways, but the byways. Hence we have chapters on the relation of mechanics to physiology, and on the theological, animistic, and mystical points of view in mechanics. In the latter is traced the gradual transition from

regarding mechanical problems from the theological standpoint to the complete separation of physics from theology, which took place about the beginning of the present century.

The translator merits commendation for the excellent work he has done. A Germanism occurs here and there, it is true, but not enough to mar the reader's enjoyment. His annotations, too, are useful and show care and research. The book is handsomely printed, and deserves a warm reception from all interested in the progress of science.

T. W. WRIGHT.

A Text-Book on Electromagnetism and the Construction of Dynamos. Vol. I. By DUGALD C. JACKSON, B.S., C.E., Professor of Electrical Engineering in the University of Wisconsin. 8vo, pp. 281. New York, Macmillan & Co.

The large number of works upon dynamo-electric machinery and kindred subjects in electrical engineering which are now appearing and about to appear (for we hear from various publishers of further works now in press and in preparation) leads us to inquire the reason for such literature. Most of these books cover identically the same ground, and many of the authors so state in their prefaces. The cause is easily traced to the rapid growth of the electrical industries during the last decade, which has developed a demand for practical information on electrical subjects, and indirectly occasioned a stimulus to scientific investigation and study of electricity from a purely scholarly standpoint. This demand has for the most part been met with general treatises, the authors of which, endeavoring to cover the entire field, have covered what they could, and staked out claims for the remainder. These general treatises often contain a great deal that is of value, but are not in every way satisfactory. It is from an appreciation of this fact, and an honest belief that they may be able to do better, that authors have been led to the production of such books as the one in hand. Many fail; those who succeed generally do so by specializing, and by giving a complete and logical exposition of some one branch of the subject previously treated in a fragmentary manner. It is, therefore, with some apprehension, that we take up a book on "Electromagnetism and the Construction of the Dynamo," fearing that in the same volume we may find Maxwell's theory of magnetism, and a detailed description of forms of dynamos, construction of commutators, etc. However, we are relieved to find the title a misnomer and that the book is on electromagnetism and its relation to the dynamo. The question of design is not taken up; no cuts or description of typical machines appear; details of construction are entirely passed over; and the book is devoted to the principles of the magnetic circuit and of the dynamo.

The treatment of the magnetic circuit in the first chapter is particularly clear, and in a few pages the reader is able to gain a knowledge of permeability, reluctance, magnetomotive force, and magnetization. Simple electromagnets are treated in the second chapter, and magnetic properties of iron in the third. The results of the researches of Ewing, Hopkinson, Steinmetz, and others is given in brief, and illustrated by typical curves. Most of these curves are plotted to show the relation between the permeability and the induction, rather than the relation between induction and magnetizing force, which is more usual, and therefore preferred. Fig. 25, *Miscellaneous Curves*, is to be criticised. In this figure curves are plotted in which the co-ordinates represent B, H, I, κ, and μ. It is only after careful study that one not already familiar with such curves can tell the co-ordinates corresponding to any particular curve.

The explanation of the establishment of electric pressure is well given in a separate chapter, but contains some analytical expressions for the electromotive force which seem hardly called for. The subject of magnetic leakage is well treated, the formulæ of Forbes and others being given and derived for several cases. The determination of the reluctance between two parallel cylinders is given in full and seems a little out of place in an elementary work of this kind, involving as it does the formulæ of Poisson and Laplace.

The subject of armature reactions and the so-called "cross" and "back" turns is given the prominence which it deserves, and various methods of compensation for the cross-turns are discussed, particularly the arrangement of compensating series coils devised by Professor Ryan.

In the chapter on characteristic curves and regulation, the graphical methods of compounding are particularly valuable, not so much perhaps for their practical bearing as for the insight they give into the action of a dynamo. The book closes with a chapter on efficiencies and one on multipolar dynamos.

The author draws largely from S. P. Thompson and Ewing, to whom due credit is given. The reader is usually referred to some standard work for such proofs as are omitted. The explanations are clear and for the most part adequate. Although written primarily for a text-book, the work is useful for reference and is accordingly of value to the engineer. It can be recommended to students in electrical engineering.

F. BEDELL.

Resistance of Ships and Screw Propulsion. By D. W. TAYLOR. 8vo, pp. ix+239. New York, Macmillan & Co., 1893.

Among the various contributions to this subject which have recently appeared, the present may be considered as one of the most notable. It

opens with a general description of the main features of ship resistance. Free use is made, and duly credited, of the papers of the Froudes in the transactions of the Institute of Naval Architects. Based on the principles herein set forth, an approximate expression is derived for the natural or tow-rope resistance. This is of two terms, one giving the frictional and the other the wave-making resistance. Two controlled constants are involved, one being the coefficient of frictional resistance, and the other a constant relating the wave-making resistance to the fourth power of the speed. The application of the formula depends, of course, on the proper control of the constants, some precedents for which are given in a later chapter.

Chapter II. is taken up with a new development of one of the methods for the treatment of the theory of the screw propeller.

Such theories in general may be divided into two classes.

(1) Those in which the quantities involved are the mass of water acted on, and the acceleration given to this water.

(2) Those in which the quantities involved are the geometry and movement of the propeller itself, and the amount and distribution of pressure over its surface as it moves through the water.

Theories of both classes are incomplete: those of the first, for the reason that we are not able to ascertain in any given case either the amount of water actually acted on, or the acceleration effected; those of the second, because the amount and distribution of pressure cannot be accurately determined. Those of the first class have been more commonly in use. In 1878, however, the late William Froude published a notable paper in the transactions of the Institute of Naval Architects, in which was sketched from the second standpoint, the foundation of a theory for the action of an element of a screw propeller. This has been followed by a few papers from other writers bearing on the same general topic.

Not until the present work, however, has there been a systematic attempt to develop into a basis of design the theory from this standpoint.

Briefly stated it may be said that the method used involves first the assumption of two controlled constants; one giving the relation between unit normal pressure and velocity, and the other, that between unit frictional resistance and velocity. The torque, thrust, and efficiency may then be expressed as a function of speed, the geometry of the propeller, and these constants. The geometry of the propeller is introduced in two elements, first the diameter as a dimension, and second, certain functions of the geometrical form which are rendered independent of actual dimension, and are denominated "characteristics." The actual surfaces being non-algebraic, these characteristics are expressed in the form of integrals whose values are found by approximate methods from the drawings of the

propeller. The performance of any propeller being expressed in terms of these known functions and of the two unknown constants, it becomes possible by comparison with experimental results to determine values of the latter, and thus to obtain the necessary control.

It may be noted that in the computations for characteristics, the driving face only of the propeller is involved. The value of the constants found will, however, include the effect of the thickness on the back, and may therefore be considered as means for the entire surface.

The constants being thus determined, the formulæ become appropriate for the purposes of design under similar conditions.

The same general method provides, also, a means of determining the net resultant stress on the root of the propeller blade, and hence gives the necessary data for the design for strength.

Another important feature of the work is the method developed in Chap. IV. for the analysis of the results of trial trips, and the distribution of the power among the several components. A comprehensive outline of the method would be too long for the present limits, but the results obtained are as follows: —

The assumption and consequent elimination of the load engine friction.

The determination of the initial engine friction, and the consequent elimination of the engine friction entirely.

The determination of the power required to overcome the resistance and friction of the propeller.

The subdivision of the remaining thrust power, among the following components: — (1) That required to overcome the skin resistance of the ship. (2) That required to overcome the wave-making resistance of the ship. (3) The power involved in the thrust deduction.

The value of the wake factor, and the various efficiencies of the propeller also appear in the course of the analysis. The methods used in this analysis are highly ingenious, and with proper care will undoubtedly give valuable information relative to the distribution of power. From the very nature of the case, however, the analysis involves certain assumptions and several controlled constants. The propriety of the former and proper values of the latter can only be determined by experience in the application of the method to the analysis of varying cases.

As a whole, the mode of analysis is, so far as I know, the first by means of which the indicated horse power, as given by experimental results, may be subdivided in so great detail.

In Chap. V., an account is given of various methods for estimating the power required for the propulsion of a ship at a given speed. The different methods in common use are explained, and a series of tables and graphical data are given for the ready application of Froude's law of

comparison. The method by the use of the Admiralty $D^{\frac{2}{3}}$ coefficient is characterized as very untrustworthy. It may be assumed that reference is had to the method of use without proper means of control for the constant; for, as it is well known, the use of this formula with the *same* values of the constant for *similar* ships at *corresponding* speeds, will give results identical with those obtained by Froude's law of comparison as explained by the author. As a matter of fact, the use of the $D^{\frac{2}{3}}$ formula with the constant thus controlled is but one of the many forms in which this law may be expressed.

The most general of the law of comparison is as follows: — Let the resistance of a ship consist of such terms that it is capable of expression in the following form: —

$$R = \Sigma A L^{3-\frac{n}{2}} v^n;$$

where A is a constant for any one form of ship, L is a linear dimension of the ship, v the speed, and n may have, within certain limits, any value, either whole or fractional. Such conditions being fulfilled, it is readily shown that similar ships (those wherein only L varies) at corresponding speeds (those in the ratio of the square roots of the linear dimensions) have resistances as the cubes of their linear dimensions. In fact, one of the simplest conceptions of the law of comparison is that it virtually assumes the resistance of a ship to be capable of expression by the sum of a series of terms as above.

The use of the $D^{\frac{2}{3}}$ formula may be readily seen to be merely a special case of the application of this general form.

In addition to these methods, the author gives another called the "independent" estimate method. This is based on the formula for resistance developed in Chap. I., together with certain assumptions relative to propeller efficiency, engine friction, etc. This method, provided the constants are properly controlled, would give results valuable for comparison with those obtained by the use of Froude's law.

As a whole, the work is an exceedingly valuable contribution to the subject. Many of the methods used are characterized by originality combined with great ingenuity and elegance. As aids in the practical application of the theories and methods developed, the book abounds throughout with tables and graphical data. In connection with this application, the only caution to be observed is one inseparable from the nature of the subject; that is, that any applied theory resting on a series of assumptions, not capable of *a priori* proof, and involving a considerable number of controlled constants, must necessarily be used with care and only applied to the extent justified by the amount of control to which the constants have been subjected.

W. F. DURAND.

Alternating Currents: An Analytical and Graphical Treatment for Students and Engineers. By FREDERICK BEDELL, Ph.D., and ALBERT C. CREHORE, Ph.D. New York, W. J. Johnston Co.; London, Whittaker and Co. *Second edition.*

The second edition of this book is not materially different from the first, a review of which appeared in the PHYSICAL REVIEW, No. 1.